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ON ELECTROSYNTHESES BY THE DIRECT UNION OF ANIONS OF WEAK ORGANIC ACIDS.

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In 1849 Kolbe[1] made the discovery that certain hydrocarbons are among the products of the electrolysis of fatty acid salts. The interest taken in this observation was enhanced by the belief that these hydrocarbons were the long-sought alcohol radicals, obtained at last in the free state by the decomposing action of the electric current. With the development of the theory of carbon compounds a different interpretation of these facts became necessary, and it was soon found that these supposed alcohol radicals were compounds, in each molecule of which two radicals of the same kind were combined. The equation representing such electrolyses,

$$2RCO_2M' = R_2 + CO_2 + 2M',$$

was therefore the expression of a synthesis as well as a decomposition.

Since these early experiments by Kolbe, the work of many chemists has confirmed the rule that the electrolysis of salts of monobasic organic acids may in general be expected to yield a certain quantity of a compound R_2, formed by the union of residues R from two anions RCO_2—, which simultaneously lose carbon dioxide. But the anions of organic acids, like those from inorganic acids, have at the same time a strong tendency to react

[1] Ann. Chem. (Liebig) **64**, 339.

with the water of the solution in which they find themselves. Consequently a large part of the original acid is always regenerated in such experiments, and the quantity of hydrocarbons synthesized in a given time cannot be directly calculated from a knowledge of the strength of the current by an application of "Faraday's Law."

Recent investigations by Crum-Brown and Walker[1] have shown that the conditions are most favorable for the reaction,

$$2RCO_2 - = R_2 + 2CO_2,$$

when the solutions employed are concentrated and the electrical density at the positive electrode is high. These chemists also made a new and interesting application of this general reaction in the synthesis of the ethers of certain aliphatic dibasic acids, in which sodium alkyl salts of dibasic acids, lower in the homologous series, were used as the starting-point,

$$2C_2H_3CO_2(CH_2)_xCO_2Na = (CH_2)_x(CO_2C_2H_5)_2 + 2CO_2 + 2Na.$$

Thus sodic ethylic malonate gave a 60-per cent. yield of succinic ether, and sodic ethylic succinate in turn gave a 35-per cent. yield of adipinic ether, the yields decreasing as the masses of the molecules involved became greater.

In volume 15, p. 523, of this journal, in an article on "A New Class of Organic Electro-syntheses," S. P. Mulliken has shown that in the electrolyses of certain weak organic acids which do not contain the carboxyl group, a fraction of the anions unite directly in pairs without any previous splitting, according to the equation,

$$2RM' = R_2 + 2M'.$$

Three cases of this kind are described in detail by Mulliken; viz. a synthesis of ethane-tetracarbonic ether from the sodium salt of malonic ether; of ethane-hexacarbonic ether from methin-tricarbonic ether; and of tetracetylethane from a concentrated solution of acetylacetone in weak alcohol.

The experimental work of the author is a continuation of this investigation of Dr. Mulliken, and was undertaken at his suggestion, with a twofold purpose. One object was to ascertain how general a phenomenon the pairing of anions from weak organic acids is. With this end in view the following bodies were electrolyzed: methyl-malonic ether, ethyl-malonic ether, benzyl-malonic

[1] Ann. Chem. (Liebig) **261**, 107.

ether, acetyl-malonic ether, acetyl-benzoyl-methane, cyan-acetic ether, aceto-acetic ether, acetone-dicarbonic ether, phenyl-methyl-pyrazolon, phthalimide, succinimide, acetamide, and benzamide. Several well known acidic types, like that of the nitro-paraffins, are not represented in this list, it being possible in the time at my disposal to study only a few of the most important and accessible classes of compounds.

The other question which I have tried to settle has reference to the nature of the reaction which leads to the formation of the compounds R_2. In nearly all electrosyntheses some oxygen is set free at the positive electrode, and when alkali salts in alcoholic solution are being electrolyzed, the oxidation of organic matter is sometimes sufficient to produce a very noticeable precipitate of mono-sodium carbonate. Since it is known that the conductivity of the weak acids here investigated is extremely poor, it would appear, *à priori*, that some of the syntheses described might be due to oxidation of the replaceable hydrogen in two molecules of acid according to the equation,

$$2RH + O = R_2 + H_2O,$$

and not to the reaction,

$$2RH = R_2 + H_2,$$

as previously assumed. In fact, in a discussion before the Chemical Society, in February, 1893, the action of electrolytic oxygen was suggested by Armstrong[1] as the most probable explanation of the electrosyntheses of Crum-Brown and Walker. Dr. Walker in reply stated that he did not consider it probable that the formation of synthetic ethereal salts during the electrolysis was due to oxidation at the anode. Murrey[2] had shown in case of the electrolysis of potassium acetate that there was no sort of proportionality between complete oxidation to carbonic anhydride and "partial oxidation" to ethane, as might be expected if the formation of ethane was due to oxidation. The conditions of the electrolysis found most favorable for the production of synthetic products were such as would almost insure complete oxidation of the dissolved substance, if the primary action was the decomposition of water into oxygen and hydrogen.

While there doubtless are cases in which electrolytic oxygen does produce the same compounds that would result from the

[1] Chemical News **67**, 129. [2] J. Chem. Soc. 1892, 10.

direct union of organic anions, one such case being described in the present article, my work gives new proof in other cases that electrosynthesis by the direct union of anions is *not* an oxidation phenomenon.

Oxidation Experiments with Malonic Ether, Methin-tricarbonic Ether, and Acetyl-acetone.

The oxidizing agents employed in these experiments were hydrogen peroxide, potassium permanganate in sodium hydrogen carbonate solution, and an acetic acid solution of chromic acid. The first two of these oxidizing agents were selected because it seemed probable that their action would most closely resemble that of the nascent oxygen present in the electrolytic cell. The use of an acid solution of chromic acid was an attempt to vary the conditions of oxidation, after it had been proved that neutral and alkaline oxidizing agents did not give the same products as electrolysis.

10 grams of malonic ether and 50 grams of hydrogen peroxide (2-per cent. solution) were heated on the water-bath for 12 hours. The malonic ether had completely disappeared at the end of this time. The solution was then evaporated to dryness on the water-bath. The residue proved to be pure malonic acid melting at 133°, and there was no indication that any ethane-tetracarbonic ether had been formed.

To determine what action hydrogen peroxide would have on ethane-tetracarbonic ether, if this should be formed from the malonic ether, the following experiment was carried out:

1.2 grams of ethane-tetracarbonic ether were heated with 30 grams of hydrogen peroxide on a water-bath for 15 hours. The ether was completely dissolved, but, on cooling, separated out in fine needles which proved to be unchanged ethane-tetracarbonic ether.

The surprising ease with which malonic ether was saponified by a weak solution of hydrogen peroxide at this comparatively low temperature led me to study the action of distilled water upon it under the same conditions.

5 grams of malonic ether and 30 grams of distilled water were heated on the water-bath for 12 hours and frequently shaken. At the end of this time the ether had completely disappeared. The solution was evaporated on the water-bath to dryness. The

residue proved to be pure malonic acid melting at 133°. During the evaporation a slight odor of acetic acid was present.

Hjelt[1] in some experiments on the action of water on malonic ether, heated malonic ether with water in a sealed tube at 150° and obtained as a result malonic acid, acetic acid, and acetic ether. From this he concluded that malonic ether is first changed to acetic ether and the latter to acetic acid. But from my experiments on malonic ether at temperatures below 100° it appears that the ether is first completely saponified to malonic acid, which at a higher temperature loses carbon dioxide, forming acetic acid. The presence of acetic ether in experiments with sealed tubes can be readily explained as the result of the action of acetic acid on the alcohol from the malonic ether.

The employment of acid sodium carbonate with potassium permanganate in oxidation experiments, which has been much used by von Baeyer in his work on the hydrophthalic acids, was found very convenient, as such a solution contains no mineral acid or caustic alkali which would saponify the ethers experimented with. Experiments on formic acid showed that in such a permanganate solution, two molecules of potassium permanganate contain four available atoms of oxygen. 100 grams of a saturated solution of sodium hydrogen carbonate were placed in a flask with ten grams malonic ether. A two-per cent. solution of potassium permanganate was then run into the mixture with constant agitation, in quantity sufficient to oxidize one atom of hydrogen in each molecule of malonic ether. After standing for several hours the oxidized mixture was filtered and extracted with ether. The ethereal extract contained 8.3 grams of malonic ether, but no ethane-tetracarbonic ether. An examination of the aqueous solution which had been extracted with ether showed that oxalic acid was the chief product of the oxidation of malonic ether. The addition of potassium permanganate to a mixture of malonic ether and sodium hydrogen carbonate until a permanent color is produced, causes the complete destruction of the malonic ether without formation of any ethane-tetracarbonic ether.

In the oxidation by chromic acid, 2.07 grams of chromic acid dissolved in 20 grams of acetic acid were added to 10 grams of malonic ether in 20 grams of acetic acid. The solution was allowed to stand for three hours, filtered, acetic acid removed by evapora-

[1] Ber. d. chem. Ges. **13**, 1949.

tion, and the residue distilled. No ethane-tetracarbonic ether had been formed.

The oxidation experiments on methin-tricarbonic ether and acetyl-acetone, which, on electrolysis, yield ethane-hexacarbonic ether and tetra-acetyl-ethane respectively, were made in the same manner as those on malonic ether, and do not require detailed description.

The partial saponification of methin-tricarbonic ether gives malonic ether, and its oxidation-products were found to be the the same as given by this body. They contained no trace of ethane-hexacarbonic ether.

The results of the oxidation experiments on acetyl-acetone and aceto-acetic ether were also of a negative character.

Constitution of Ethane-hexacarbonic Ether.

In the account of his synthesis of this new hexacarbonic ether, Mulliken[1] employs the following equations to account for its formation:

$$2\ \begin{matrix} C<^{OC_2H_5}_{ONa} \\ \| \\ C(CO_2C_2H_5)_2 \end{matrix} = Na_2 + 2C\equiv(CO_2C_2H_5)_3$$

$$\rightarrow \begin{matrix} C\equiv(CO_2C_2H_5)_3 \\ | \\ C\equiv(CO_2C_2H_5)_3 \end{matrix}.$$

While from analogy with the reaction that takes place in the synthesis of ethane-tetracarbonic ether from malonic ether, in which the carbon atoms of two anions unite, the correctness of this equation appears almost certain, the constitution of ethane-hexacarbonic ether nevertheless requires additional proof; for several cases have been lately described by Michael,[2] Nef,[3] and Claissen,[4] in which the sodium in compounds of this class may be directly replaced by an acid radical. If it were possible for the reaction to take this second course, a compound having the following symbol would result,

$$\begin{matrix} (C_2H_5O_2C)_2 \\ C_2H_5O \end{matrix}\!\!>\!C-O-O-C\!<\!\!\!\!\!\!\begin{matrix} (CO_2C_2H_5)_2 \\ OC_2H_5 \end{matrix}.$$

Saponification of the ether under consideration appeared to offer the easiest means of determining its constitution. If it is a true

[1] This Journal **15**, 527.
[2] Ann. Chem. (Liebig) **266**, 79.
[3] *Ibid.* **14**, 489–491.
[4] *Ibid.* **277**, 166.

hexacarbonic ether, saponification should give a salt of the corresponding acid, or bodies closely related to it; while, if its constitution were represented by the less probable formula, the action of potash would be likely to split the molecule into two molecules of the original substance, which as Conrad and Guthzeit[1] have shown, on saponification gives potassium malonate,

$$CH(CO_2C_2H_5)_3 + 4KOH = CH_2(CO_2K)_2 + 3C_2H_5OH + K_2CO_3.$$

The ethane-hexacarbonic ether which I saponified was prepared from the sodium salt of methin-tricarbonic ether by Mulliken's method. It melted at 102° and distilled under a pressure of 17 mm. above 180°. The average yield amounted to about 10 per cent. of the weight of the sodium salt electrolyzed. It was found necessary to use a very concentrated solution of potash for the saponification, as it is scarcely attacked by weak solutions even when the potash is much in excess of the theoretical quantity. The ether was therefore dissolved in 10 parts of absolute alcohol, 10 times the calculated quantity of a 30-per cent. alcoholic solution of potash added, and the mixture warmed on a water-bath with return condenser for three and one half hours. The potassium salt soon began to separate from the solution, and when the saponification was complete it was separated by filtration, washed with alcohol, dissolved in a small quantity of water, and then crystallized by evaporation in a vacuum-desiccator over sulphuric acid. Fine rhombohedral crystals were obtained, some of which had a length of ½ cm. This salt was very stable and could be heated as high as 250° for hours without decomposition. It attracts moisture rapidly from the atmosphere and is very soluble in water. The crystals after being dried to constant weight over sulphuric acid were found to contain water of crystallization, all of which was lost at 120°.

I. 0.2956 gram of potassium salt dried at 120° lost 0.0273 gram of H_2O.

II. 0.2545 gram of potassium salt dried at 120° lost 0.0233 gram of H_2O.

III. 0.3267 gram of potassium salt dried at 120° lost 0.0299 gram of H_2O.

	Calculated for $C_2H_2(CO_2K)_4 + 2H_2O$.	Found. I.	II.	III.
H_2O	9.13	9.24	9.16	9.14

[1] Ann. Chem. (Liebig) **214**, 33.

A determination of potassium in this salt by conversion into potassium sulphate gave the following results:

I. 0.2956 gram of crystallized salt gave 0.2616 gram K_2SO_4.

II. 0.2545 gram of crystallized salt gave 0.2241 gram K_2SO_4.

III. 0.2777 gram of crystallized salt gave 0.2612 gram K_2SO_4.

	Calculated for $C_2H_2(CO_2K)_4 + 2H_2O$.	Found. I.	II.	III.
K	39.67	39.69	39.53	39.69

From these determinations it is evident that the compound analyzed was not the potassium salt of ethane-hexacarbonic acid, but of ethane-tetracarbonic acid which had been formed from the ethane-hexacarbonic ether by the reaction,

$$(C_2H_5CO_2)_2 \equiv C - C \equiv (CO_2C_2H_5)_2 + 8KOH = (KCO_2)_2CH.CH.(KCO_2)_2 + 2K_2CO_3 + 6C_2H_5OH.$$

The identification of this salt was completed by converting it into the corresponding silver salt, which on treatment with ethyl iodide gave the well-known ethane-tetracarbonic ether. The same salt was also prepared by saponification from a pure specimen of ethane-tetracarbonic ether, and analyzed with the following results:

I. 0.5233 gram of crystallized salt contained 0.0478 gram H_2O.

II. 0.3297 gram of crystallized salt contained 0.0303 gram H_2O.

III. 0.5233 gram of crystallized salt contained 0.4117 gram K_2SO_4.

IV. 0.3297 gram of crystallized salt gave 0.2912 gram K_2SO_4.

	Calculated for $C_2H_2(CO_2K)_4.2H_2O$.	Found. I.	II.	III.	IV.
H_2O	9.13	9.21	9.21	...	...
K	39.67	...	...	39.60	39.71

Ethane-tetracarbonic Acid.

Conrad and Bischoff[1] have studied the action of potash upon ethane-tetracarbonic ether and found that the resulting potassium salt, when decomposed with acetic acid, gave an oily substance, from which they separated ethenyl-tricarbonic acid melting at 155°. Saponification of the ethane-tetracarbonic ether by boiling hydrochloric acid gave the same product:

$$(C_2H_5CO_2)_2CH - CH(CO_2C_2H_5)_2 + H_2O = (HCO_2)_2CH - CH_2CO_2H + CO_2 + 4C_2H_5OH.$$

[1] Ann. Chem. (Liebig) **214**, 71.

Recently Buchner,[1] by saponifying ethane-tetracarbonic ether, obtained a substance melting at 167°–169° which, on heating, was transformed into succinic acid. Buchner's work was not known to me when I was engaged in these experiments, and as his description of the properties of the acid is very incomplete, my observations in regard to its formation and its properties may be of some interest. Desiring to ascertain whether, as the experiments of Conrad and Bischoff seemed to show, ethane-tetracarbonic acid is really so unstable that it cannot be liberated without losing carbon dioxide and being converted into a tri- or dibasic acid, 0.7892 gram of the potassium salt of ethane-tetracarbonic acid was dried at 130° and dissolved in 20 cc. of distilled water. Just enough sulphuric acid was then added to combine with the potassium of the salt, the flask being connected with potash-bulbs by means of a long tube half filled with calcic chloride. After the mixture had been allowed to stand several hours, air was drawn through the apparatus. No carbon dioxide had been given off. The mixture was then warmed on the water-bath for one hour. In this time the acid had lost 17.16 per cent. of carbon dioxide. Conversion of the ethane-tetracarbonic acid into the ethenyl-tricarbonic acid would involve a loss of 12.29 per cent. of carbon dioxide. Ethane-tetracarbonic acid is therefore quite stable at ordinary temperatures, although readily splitting off carbon dioxide in the manner indicated by Conrad and Guthzeit when warmed. By heating the aqueous solution as long as the potash-bulbs increased in weight, it was found that 0.1924 gram of carbon dioxide had been lost; a loss which closely corresponds to that (0.1939 gram) required by the equation,

$$C_2H_2(CO_2H)_4 = C_2H_4(CO_2H)_2 + 2CO_2.$$

The contents of the flask at the close of the experiment were extracted with ether. The ethereal solution, on evaporation, gave a residue of crystals of succinic acid, melting at 185°.

The preparation of free ethane-tetracarbonic acid is easily accomplished by adding to a 15-per cent. aqueous solution of its potassium salt the calculated quantity of sulphuric acid and then allowing the solution to evaporate spontaneously. All heating must be carefully avoided. The residue is extracted with ether to separate the acid from the potassium sulphate.

[1] Ber. d. chem. Ges. 25, 1157.

The ethereal solution on evaporation deposits the acid in beautiful tablets, apparently of the monoclinic system, which melt with decomposition at 169°–171°. The fused mass after solidification remelts above 180° and consists of succinic acid. Ethane-tetracarbonic acid is readily soluble in water, alcohol and ether, but almost insoluble in benzene and acetic acid. Its clear, colorless crystals gradually break down to a white powder on exposure to the air. Combustions of the acid gave the following results:

I. 0.2504 gram of the acid dried *in vacuo* gave 0.3213 gram CO_2 and 0.0732 gram H_2O.

II. 0.2488 gram of the acid dried at 100° gave 0.3163 gram CO_2 and 0.0726 gram H_2O.

	Calculated for $C_2H_2(CO_2H)_4$.	Found. I.	II.
Carbon	34.95	34.99	34.67
Hydrogen	2.92	3.24	3.24

Reagents gave the following precipitates with a solution of its potassium salt:—

Argentic nitrate: White precipitate soluble in ammonia, not reprecipitated by nitric acid.

Barium chloride: White precipitate soluble in nitric acid.

Calcium chloride: White precipitate.

Plumbic acetate: White precipitate insoluble in boiling water.

Mercurous nitrate: White precipitate insoluble in boiling water.

Mercuric chloride: White precipitate on warming the solution.

Ferrous sulphate: Light-brown precipitate, does not appear at first.

Zinc sulphate: White precipitate which increases on heating.

Magnesium sulphate: No precipitate.

Electrolysis of Methyl-malonic Ether.—(Dimethyl-ethane-tetracarbonic Ether).

$$2\ \begin{matrix} CH_3CCO_2C_2H_5 \\ \| \\ C_2H_5OCONa \end{matrix} = Na_2 + 2-C\begin{matrix} CH_3 \\ \diagdown\!\!\diagup \\ (CO_2C_2H_5)_2 \end{matrix}$$

$$\rightarrow \begin{matrix} CH_3 \\ \diagdown \\ (CO_2C_2H_5)_2 \end{matrix}\!\!\diagup\!\!\diagdown C - C\begin{matrix} \diagup\!\!\diagdown \\ CH_3 \\ \diagdown\!\!\diagup \\ (CO_2C_2H_5)_2 \end{matrix}$$

In this electrolysis, as well as in those which will be spoken of further on, the electrolyte was placed in a small porous cylindrical cell. The anode, a spiral of thick platinum wire, was suspended

in this cylinder, which was itself placed within a beaker of about the same height, but of slightly greater diameter, filled with the solvent used for the experiment. The cathode, a large piece of platinum foil, was fitted close to the sides of the beaker and surrounded the inner vessel. The supply of electricity was obtained from a storage battery having a maximum electromotive force of about 40 volts. When aqueous solutions of metallic salts were contained in the cell it was often necessary to reduce the current by placing a rheostat in the circuit. Three amperes was the strongest current used in any experiment. A more powerful current caused too much heating, even when the solution was well cooled by ice-water.

60 grams (one mol.) of methyl-malonic ether were dissolved in 75 grams of absolute alcohol containing 6.6 grams (one atom) of metallic sodium. This solution was subjected to the action of a current of $\frac{1}{3}$ of an ampere for 28 hours, that is, for a time slightly greater than would theoretically be required completely to decompose the sodium salt placed in the cell. The porous cell served a useful purpose by preventing the saponification of the ethereal compounds, the alkali produced by the electrolysis all accumulating in the outer vessel.

In the experiments on methyl-malonic ether a total of 190 grams of substance was consumed. After electrolysis the alcoholic solution was neutralized with dilute sulphuric acid, the alcohol evaporated on the water-bath; the residue extracted with ether and water; the ethereal extract dried with calcium chloride; the ether removed by distillation; and the resulting oil then distilled under reduced pressure. Two grams of oil were thus finally obtained which boiled under a pressure of 15 mm. at 167°. The principal portion of the oil boiled at 110° under the diminished pressure and was methyl-malonic ether. The molecular weight of the higher-boiling portion was determined by the method of Raoult:

Wt. of substance.	$t°-t°'$.	Benzene.	Mol. wt. found.
0.3095 gram,	0.371	13.2624 grams.	314
0.6955 "	0.801	"	321
0.9618 "	1.073	"	341

The oil was then analyzed.

I. 0.2120 gram substance gave 0.4160 gram CO_2 and 0.1368 gram H_2O.

II. 0.4640 gram substance gave 0.9130 gram CO_2 and 0.2936 gram H_2O.

	Calculated for $(CH_3)_2CH_2(CO_2C_2H_5)_4$.	Calculated for $C_{15}H_{26}(CO_2C_2H_5)_4$.	Calculated for $2C_{15}H_{26}(CO_2C_2H_5)_4 + (CH_3)_2C_3(CO_2C_2H_5)_4$.	Found. I.	Found. II.
Carbon	55.49	52.68	53.71	53.63	53.66
Hydrogen	7.53	6.89	7.13	7.17	7.03

It will be seen from these figures that the oil boiling at 167° under reduced pressure contained very nearly the quantity of carbon and hydrogen that would be found in a mixture of two molecules of ethane and one molecule of dimethyl-ethane-tetracarbonic ethers. That such a mixture was actually present was rendered probable from the result of the molecular weight determinations, for such a mixture would have a molecular weight of 327, while the mean result found was 325.

The formation of this mixture is easily explained. The methyl-malonic ether used was prepared in the usual way from malonic ether, sodium ethylate and methyl iodide. The boiling-points of methyl-malonic ether and of malonic ether differ from each other by only about one degree, so that it is impossible to separate the two by the most careful fractionation. It is stated by Mulliken that in the electrolysis of sodium malonic ether the yield of ethane-tetracarbonic ether is 25 per cent. In my experiments only about 2 per cent. of the methyl-malonic ether used was converted into the oil boiling at 167° under reduced pressure. From this experiment and that which follows there is no doubt that electrosyntheses from the homologues of the malonic ether are made less readily than when malonic ether itself is used as the starting-point. Consequently, in the electrolysis just described a considerable part of the malonic ether present as an impurity in the methyl-malonic ether was changed into ethane-tetracarbonic ether, and its quantity was greater than that of the desired product.

By taking advantage of the remarkable stability of ethane-tetracarbonic ether towards weak alcoholic potash, which has already been referred to in this paper, it was found possible to separate the mixture of dimethyl-ethane-tetracarbonic and ethane-tetracarbonic ethers by partial saponification. The portion of the high-boiling oil recovered from the molecular weight determinations was warmed with five times the calculated quantity of a ten-per cent. alcoholic solution of potash for three hours. An insol-

uble potassium salt separated out in distinct needles. This was filtered off and washed with alcohol. Only about one-third of the oil had been saponified. The salt was dried at 160° and the potassium determined as sulphate.

I. 0.1138 gram substance gave 0.1026 gram K_2SO_4.

II. 0.1282 gram substance gave 0.1156 gram K_2SO_4.

	Calculated for $(CH_3)_2C_2(CO_2K)_4$.	Found. I.	II.
K	40.41	40.49	40.48

Electrolysis of Ethyl-malonic Ether (Diethyl-ethane-tetracarbonic Ether).

$$2\ \begin{matrix} C_2H_5CCO_2C_2H_5 \\ \| \\ C_2H_5OCONa \end{matrix} = Na_2 + 2 - C\begin{matrix} \diagup C_2H_5 \\ \diagdown (CO_2C_2H_5)_2 \end{matrix}$$

$$\rightarrow (C_2H_5CO_2)_2\begin{matrix} \diagdown C_2H_5 \\ \diagup \end{matrix} C - C\begin{matrix} \diagup C_2H_5 \\ \diagdown (CO_2C_2H_5)_2 \end{matrix}.$$

This electrolysis was conducted in the same manner as that of the methyl-malonic ether.

1.5 grams (½ atom) metallic sodium were dissolved in 50 grams of absolute alcohol, and when the solution had become cold, 25 grams of ethyl-malonic ether were added to it and the solution placed in a porous cell. A current of ½ ampere was passed through the solution for 17 hours. The mixture was then neutralized with dilute sulphuric acid mixed with water, extracted with ether, and the residual oil obtained from the extract distilled under reduced pressure. About 0.5 gram of this oil boiled above 150° under a pressure of 15 mm. The remainder was ethyl-malonic ether.

A molecular-weight determination of the oil boiling above 150°, by Raoult's method in a benzene solution, indicated that it was a mixture of diethyl-ethane-tetracarbonic ether and ethyl-malonic ether.

Wt. of substance.	Benzene.	$t°-t°'$.	Mol. wt. found.
0.4025 gram.	14.45 grams.	0.45°	309
0.2583 (recovered).	14.313	0.293°	309

The molecular weight of ethyl-malonic ether is 188, and that of diethyl-ethane-tetracarbonic ether is 374. The material used in the above molecular-weight determinations was saponified by boiling with five times the calculated quantity of a ten-per cent. solution of potash, and the potassium salt obtained dried at 160° and analyzed.

I. 0.2121 gram of this salt gave 0.1779 gram K_2SO_4.
II. 0.1373 gram of this salt gave 0.1152 gram K_2SO_4.

	Calculated for $(C_2H_5)_2C_2(CO_2K)_4$.	Found. I.	II.
K	37.67	37.65	37.67

These results show that the anticipated reaction, $2C_9H_{15}O_4Na = Na_2 + C_{18}H_{30}O_8$, takes place when ethyl-malonic ether is electrolyzed, but that the yield of diethyl-malonic-tetracarbonic ether is very small, amounting, according to this experiment, to only 2 per cent. of the weight of the ether electrolyzed.

Electrolysis of Benzyl-malonic Ether.

2.1 grams ($\frac{3}{4}$ atom) of metallic sodium were dissolved in 35 grams of absolute alcohol, and the cooled solution mixed with 30 grams (one mol.) benzyl-malonic ether. This solution conducted very poorly, a current of $\frac{1}{10}$ of an ampere which gradually increased to $\frac{1}{20}$ of an ampere was passed through the solution for 105 hours. The oil obtained after neutralizing with dilute sulphuric acid and extracting with ether weighed about 25 grams, and was unchanged benzyl-malonic ether. Even the highest-boiling portion of this oil, when distilled under reduced pressure, was found to have a molecular weight, according to a determination by Raoult's method, as low as 225. The calculated molecular weight of benzyl-malonic ether is 250.

Electrolysis of Acetyl-malonic Ether.

The acetyl-malonic ether used for this experiment was prepared by the method of Michael[1] and boiled at 120° under a pressure of 15–17 mm. It was freed from traces of malonic ether by shaking with a solution of sodium carbonate, in which, unlike malonic ether, it is soluble, and from which it is precipitated unchanged by acids.

21 grams of acetyl-malonic ether were dissolved in 126 grams of 50 per cent. alcohol, and the electric current passed through the solution for two days. The strength of the current, which at the beginning of the experiment was $\frac{2}{10}$ of an ampere, after 20 hours had decreased to $\frac{1}{20}$ of an ampere. The anticipated product of this electrolysis, diacetyl-ethane-tetracarbonic ether, from its constitution should evidently be a neutral body and consequently

[1] This Journal **14**, 495.

insoluble in sodium carbonate, like malonic ether. The contents of the electrolytic cell were repeatedly shaken with ether and a 10 per cent. solution of sodium carbonate. All unchanged acetyl-malonic ether was dissolved by the carbonate, while the neutral compounds went into the ethereal extract. Examination of the neutral body contained in the ethereal solution proved it to be simply malonic ether. It boiled between 90°–100° under a pressure of 10 mm. and weighed 7 grams.

No evidence that the anions, the formation of which from acetyl-malonic ether might be expected, had combined with one another was found. The malonic ether obtained from this experiment may have been formed in the cell by action of water during the electrolysis, or afterwards, while the contents of the cell were being shaken with ether and sodium carbonate. As 11 grams of acetyl-malonic ether were recovered from the solution of sodium carbonate, and 7 grams of malonic ether represented 9 grams of acetyl-malonic ether, no appreciable amount of the acetyl compound electrolyzed could have been changed to other compounds.

Electrolysis of Aceto-acetic Ether.—(*Diacetyl-succinic Ether*).

$$2CH_3C(ONa):CHCO_2C_2H_5 = Na_2 + \begin{matrix} C_2H_5 - CO_2 \\ CH_3CO \end{matrix} > CH - CH < \begin{matrix} CO_2C_2H_5 \\ COCH_3 \end{matrix}.$$

20 grams of aceto-acetic ether were added to 20 grams of 50-per cent. alcohol in which 0.3 gram of metallic sodium had been previously dissolved. A current of one ampere was passed through the solution for two hours. By the electrolysis of a dilute alcoholic solution of pure aceto-acetic ether Mulliken[1] obtained a product which gave a somewhat uncertain test for diacetyl-succinic ether by Knorr's pyrrol-reaction with a pine splinter. The experiment was repeated in order to ascertain whether a larger quantity of diacetyl-succinic ether could be obtained by using the sodium salt.

At the close of the electrolysis, in which a porous cell was not used, hydrogen sodium carbonate had been deposited as an incrustation on the anode, indicating oxidation or a splitting off of a portion of the aceto-acetic ether. After neutralizing the solution with dilute sulphuric acid and extracting with ether, the oil from the ethereal extract was tested for a 1:4-diketone by boiling

[1] This Journal **15**, 532.

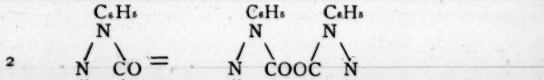
a pine-splinter in its acetic-acid solution to which ammonium acetate and dilute sulphuric acid had been added. The splinter assumed a deep red color that indicated the presence of a considerably greater quantity of diacetyl-succinic ether than was found in the case of the electrolysis of simple aceto-acetic-ether solution.

Electrolysis of Acetone-dicarbonic Ether.

It was thought probable, since diacetyl-succinic ether had been obtained from aceto-acetic ether, that an analogous diketone might be prepared by the electrolysis of acetone-dicarbonic ether. This expectation was not realized. The acetone-dicarbonic ether was prepared according to the directions of von Pechmann[1] and boiled at 145°–150° at 20 mm. pressure. The ether was converted into the potassium salt, which is easily soluble in water without decomposition.

12 grams of this salt were dissolved in 15 ccm. of distilled water and electrolyzed in a small porous cell. The current, which was at first about one ampere, entirely ceased after a few hours, all the potassium having passed into the water of the outer vessel. The oil which remained in the cell was acetone-dicarbonic ether, which distilled below 150° at 20 mm. pressure. Knorr's pine-splinter reaction for a 1 : 4-diketone gave a negative result when applied either to the oil before distillation or to the different fractions of the distillate.

Electrolysis of (1)-*Phenyl*-(3)-*methyl*-(5)-*pyrazalon.*—(*Phenyl-methyl-bis-pyrazalon*).



$$2\,C_{10}H_{10}ON_2 + O = C_{20}H_{18}O_2N_4 + H_2O.$$

3½ grams of (1)-phenyl-(3)-methyl-(5)-pyrazalon, melting at 128°–129°, were dissolved in 20 grams absolute alcohol and electrolyzed in a small beaker. The current soon increased from $\frac{1}{100}$ to $\frac{1}{8}$ of an ampere. The electrolysis was continued for 24

[1] Ann. Chem. (Liebig) **261**, 159.

hours. The solution was then of a deep red color and contained a white precipitate, which was filtered off and thoroughly washed with alcohol. This white powder, which was quite insoluble in alcohol and ether, gave the following characteristic reactions for phenyl-methyl-bis-pyrazalon: It was readily soluble in a solution of sodium hydroxide, and such a solution containing only a slight excess of alkali gave a steel-blue precipitate with ferrous salts. When boiled with ferric chloride it was changed to pyrazalon-blue. It could be heated to a temperature above 250° without showing signs of decomposition. The yield of bis-pyrazalon in this experiment amounted to ten per cent. of the phenyl-methyl-pyrazalon.

In the electrolysis of phenyl-methyl-pyrazalon we have an instance of electrosynthesis which may be explained, so far as the facts connected with it have been studied, either as the result of an oxidation or of direct union of anions. From the ease with which phenyl-methyl-pyrazalon is converted into the bis-pyrazalon by weak oxidizing agents like ferric chloride it is probable that this synthesis is, in a large measure at least, the result of oxidation. Nevertheless, the distinctively acid character of phenyl-methyl-pyrazalon renders it by no means improbable that bis-pyrazalon is at the same time formed by the second method of synthesis.

Electrolysis of Cyan-acetic Ether.

Haller[1] has carried out numerous syntheses in which the sodium salt of cyan-acetic ether was made to play the same rôle as the sodium salt of aceto-acetic ether in the familiar aceto-acetic-ether syntheses. Thus sodium cyan-acetic ether and acetyl chloride gave aceto-cyan-acetic ether, while sodium cyan-acetic ether and chlorocarbonic ether gave cyan-malonic ether. In the hope that the anions from this sodium salt might unite during electrolysis, 15 grams of the pure sodium salt are dissolved in 30 grams of distilled water, and the solution electrolyzed in a porous cell for four and one-half hours with a current of $\frac{1}{3}$–$\frac{1}{4}$ of an ampere. The contents of this cell, after neutralization and extraction with ether, consisted of an oily residue, which was distilled under a pressure of 15 mm. The distillate consisted of cyan-acetic ether and a substance boiling at 160°–165°, which solidified on cooling and melted at 67°. Analysis showed it to be cyan-acetic acid.

[1] Ann. chim. phys. **16**, 403.

There was no indication that any dicyan-succinic ether had been formed.

Electrolysis of Succinimide.

Walden[1] in his work on the affinity constants of organic acids found that an aqueous solution of this typical imide is a non-conductor of electricity. One atom of hydrogen in succinimide can, however, be readily replaced by alcoholic radicals, by treating its sodium or silver salt with alkyl iodides,[2] just as the homologues of malonic ether can be prepared by the same general method. Since Mulliken had shown that, while a solution of malonic ether does not conduct electricity, its sodium salt in alcoholic solution is a good electrolyte, it was thought possible that electrosyntheses might likewise be made from the metallic compounds of acid amides and imides. Walden in his experiments with an aqueous solution of the sodium salt of succinimide found as the value of the difference $\Delta_{32-1024}$, 20.54, which indicates that this compound is very easily decomposed by the hydrolytic action of alkali, giving rise to the sodium ammonium salt of a *dibasic acid*, *i.e.* succinic acid. It was, therefore, decided to use in my experiments the easily soluble mercury salt of succinimide. The succinimide was prepared according to a method recently described by Verley.[3] This method gives a yield of 80 per cent. and may be carried out by heating a mixture of one molecule of potassium succinate and two molecules of ammonium chloride in a glass retort immersed in a bath of fusible metal. The succinimide, which melted at 125°–126°, was converted into the mercury salt by treating a concentrated solution with mercuric oxide and recrystallizing from alcohol.[4] To test the purity of the mercury salt, two determinations of mercury were made, with the results that the first gave 50.64 and the second 50.69, instead of 50.50 of mercury as calculated for the formula $C_8H_8O_4N_2Hg$. 10.02 grams of this mercury salt were dissolved in 80 grams of water. At the beginning of the electrolysis the current was 0.5 of an ampere, but after 22 hours, when all the mercury had been precipitated, from some obscure secondary reaction it had increased to 0.6 of an ampere. The solution was evaporated and 4.79 grams of pure succinimide, melting at 125°, were recovered. Since the mercury salt electro-

[1] Ztschr. phys. Chem. **8**, 484.
[2] Comstock and Kleeberg: This Journal **12**, 493; Comstock and Wheeler: *Ibid.* **13**, 520.
[3] Bull. Soc. Chem. **10**, 690. [4] Menschutken: Ann. Chem. (Liebig) **162**, 171.

lyzed contained only 5.01 grams, the electrolysis must have proceeded as in the case of a mercury salt of an inorganic acid.

$$C_8H_8N_2O_4Hg + H_2O = 2C_4H_5NO_2 + Hg + O.$$

Electrolysis of Phthalimide.

Solutions of 10 grams (one mol.) of phthalimide melting at 220° were dissolved in 50 grams of alcohol, and 1.6 grams (one atom) of sodium dissolved in 20 grams of alcohol were mixed and electrolyzed in a porous cell by a current which was at first $\frac{1}{7}$ of an ampere. After eight hours the cell contained nothing but pure phthalimide, melting at 229°. The phthalimide used in the experiment was all recovered.

Electrolysis af Acetamide and Benzamide.

Although the concentration of the solution and the density of the current in the experiments with acetamide were very favorable for the union of the anions, as in the electrolysis of the acid imides just described, only negative results were obtained. Ten grams of Kahlbaum's acetamide, melting at 83°, were dissolved in 50 grams of distilled water. The solution showed a somewhat surprising conductivity. A current of 0.8 of an ampere was passed through the solution for 14 hours. The solution was then evaporated and nearly 10 grams of acetamide with unchanged melting-point were recovered. Fearing that the high conductivity of the acetamide might be due to an impurity being present, its mercury salt was prepared by dissolving mercuric oxide in an aqueous solution of acetamide. 22 grams of the mercury salt recrystallized from water were dissolved in 30 grams of water and electrolyzed for 51 hours. The current, which was at first only $\frac{1}{10}$ of an ampere, increased as the mercury separated out at the cathode and free acetamide was formed in the solution, until it amounted to 0.1 of an ampere. The mercury salt electrolyzed corresponded to eight grams of acetamide. Seven and one-half grams were recovered.

An attempt was made to electrolyze an alcoholic solution of benzamide and an aqueous solution of its mercury salt; but the first solution was such a poor conductor, and the mercury salt so slightly soluble in water, that no satisfactory results were obtained.

Summary.

The most important results of this investigation may be briefly summarized as follows:

1. The action of various oxidizing agents on malonic ether, methin-tricarbonic ether, acetyl-acetone, and aceto-acetic ether, does not give the compounds obtained from these bodies by electrolysis. In other words, these electrosyntheses are best explained as the result of the direct union of anions and not of an oxidation.

2. Pairing of anions has been shown to be of particularly common occurrence in the electrolysis of sodium compounds of derivatives of malonic ether. Dimethyl and diethyl ethane-tetracarbonic ethers were thus obtained from methyl and ethyl malonic ethers. The yields from these homologues were, however, much smaller than from malonic ether itself, or from methin-tricarbonic ether. The last-named compound was proved by saponification to have the constitution $C_2(CO_2C_2H_5)_6$. No indications of a pairing of anions in the electrolysis of benzyl and acetyl malonic ether could be detected.

3. Pairing of anions occurs in the electrolysis of certain compounds of the aceto-acetic-ether type (aceto-acetic ether and acetyl-acetone[1]), but failure to secure such synthetic products in the experiments with acetone-dicarbonic ether and acetyl-benzoyl-methane showed that this reaction can hardly be called a general one. The formation of bis-phenyl-methyl-pyrazalon in the electrolysis of phenyl-methyl-pyrazalon may be partly an electrolysis of this type or may be due wholly to oxidation.

4. The electrolysis of acid amides (acetamide, benzamide, succinimide and phthalimide), or their sodium or mercury salts, yields the original amides or imides without any pairing of anions.

CHEMICAL LABORATORY, CLARK UNIVERSITY, *June*, 1894.

[1] The electrical conductivity of a very pure specimen of acetyl-acetone lately prepared by Dr. Mulliken and measured by Mr. Alfred Wakeman, of the Sheffield Scientific School, was found to be no greater than that of pure water. It is, therefore, quite likely that the real electrolytes in Mulliken's electrosynthesis of tetra-acetyl-ethane were traces of salts of acetyl-acetone derived from bases in the glass of the electrolytic cell, or from the dilute alcohol used as a solvent instead of acetyl-acetone itself.

PENTOSANS IN PLANTS.

By G. de Chalmot.

I.—Pentosans in Seeds.

Are there pentosans in the plants which are formed from seeds which germinate in darkness?

It has become necessary to answer this question since Cross, Bevan and Beadle[1] in a recent article assert that the furfurol-yielding compounds in the sprouts which are developed from barley in darkness are so-called oxycelluloses, and are not pentosans. "These sprouts yield 5 per cent. of furfurol, but they do not show the usual reactions that indicate pentosans."

If this assertion be true it would be of fundamental importance. For the furfurol-yielding bodies in barley grown in light are, at least for the greater part, pentosans. The straw of small grain is in fact one of the very best materials for obtaining abundant xylose.

I found, however, that the furfurol-yielding compounds in corn and barley plants which have been developed from seeds in darkness do only very partially belong to the celluloses; far the larger part belongs to the nitrogen-free extract.

Thus I found in corn plants (seeds, stems and roots) 12 days old and which had grown in darkness, total furfurol-yielding bodies, 13.9 per cent.,[2] of which are contained in the raw fiber, 1.5 per cent. In the stems of barley plants 7 days old, from seeds grown in darkness, I found: total furfurol-yielding bodies 10.1 per cent., of which are contained in the raw fiber, 2.0 per cent.

The raw fiber was obtained by the usual Weende method. Messrs. Cross and Bevan communicated to me in a private letter that they do not use the Weende method, but use another, the main features of which are a long digestion in cold 1-per cent. sodium-hydroxide solution, and after washing out the sodium hydroxide, a second long digestion in 1-per cent. hydrochloric acid in the cold. It is very probable that they therefore do not extract as much matter as is done by the Weende method (digestion with boiling 1¼-per cent. hydrochloric acid for half an hour, and afterwards for the same time with boiling 1¼-per cent. sodium-hydroxide solution). Consequently their fiber may also

[1] Ber. d. chem. Ges. **27**, 1065.

[2] Furfurol × 2.

contain more furfurol-yielding bodies. I shall, however, prove that pentosans are contained in sprouts developed in darkness.

Stems of barley germinated and grown in darkness for seven days were twice digested with 2-per cent. ammonia solution for two hours, and after removing the liquid as much as possible, they were digested for sixty hours in the cold with 5-per cent. sodium-hydroxide solution. The solution was separated from the stems and hydrochloric acid and alcohol were added. A gum separated, which was collected, washed with alcohol, and dried over caustic potash. The dried gum was grayish in color and looked like impure wood-gum.

The very smallest amount of this gum gave a distinct color reaction with the phloroglucol reagent. The absorption-line between the lines D and E of the spectrum,[1] which is characteristic for the pentoses, was very plainly discernible.

I heated a small amount of this gum (4 grams) for six hours on the water-bath with 50 cc. of 3-per cent. sulphuric acid. The liquid was neutralized with barium hydroxide. The barium sulphate was filtered off. Phenylhydrazine hydrochloride and sodium acetate were added to the liquid, which was heated at 70° C. in the water-bath. A yellow osazone was formed after some time, which was collected on a filter. This osazone was then pressed between layers of filtering paper, purified by washing with small amounts of alcohol, and dried over sulphuric acid. This osazone melted at 140°–145° C. (uncorr.). Since I was not sure whether it was simply an impure osazone of a pentose or a mixture of osazones, I boiled 0.77 gram of the osazone with 50 cc. of water for two hours. A small part was dissolved and separated by cooling. Its melting-point was 153° (uncorr.). The rest of the osazone was once more boiled with 40 cc. of water, and the undissolved part was dried and then boiled with so small an amount of alcohol that it was nearly but not quite fully dissolved. The alcoholic liquid was poured off and allowed to stand over night. It then deposited a small amount of a tarry matter, from which it was poured off again and mixed with a small amount of water. An osazone was precipitated, which was washed with water and alcohol, and melted at 153° C. (uncorr.). The original osazone seems therefore to have consisted of the osazone of a pentose only. The melting-points of both xylosazone and arabin-osazone are 158°–160° C.

[1] Tollens: Landw. Vers. Stat. **39**, 443.

I could not find out which of the pentoses was present, since the quantities with which I worked did not admit of further tests.

The stems of barley plants grown in darkness, therefore, do contain pentosans, and once more it has been proved that vegetable matters which yield furfurol contain pentosans. It is of course not impossible that besides the pentosans there are other substances which yield larger amounts of furfurol. However, the presence of these other substances has not been proved, and I therefore for the present hold that the essential part of the furfurol which is yielded by the hydrolysis of vegetable materials with hydrochloric acid (of 12 per cent.) originates from pentosans.

The observation of Cross, Bevan and Beadle that young barley plants grown in darkness do not show the color-reaction with phloroglucol required further explanation. When I made extracts of the barley stems above referred to with diluted hydrochloric acid or diluted sulphuric acid, and when I discolored the filtrates with animal charcoal and heated them with the phloroglucol reagent, the liquid became brown, and a precipitate was formed which made invisible any red color which may have been formed. It has already been known for a longer period that hexoses form such brown dyestuffs when heated with the phloroglucol reagent. Soluble hexoses are contained in large amounts in the young barley plants, and to them this brown color and precipitate is due. It moreover seems to be mainly fructose or cane sugar which makes it impossible to recognize the pentose reaction. I took the gum which I extracted from the barley plants, and which showed the pentose-phloroglucol reaction very strongly, and heated it with the phloroglucol reagent and a little starch. I was then able to obtain a cherry-red color by heating very gently. In this case the pentose reaction (red) set in before the glucose reaction (brown). When I used instead of starch cane-sugar, I did not obtain any red color, but the liquid at once became brown. The fructose (of the cane-sugar) therefore reacts with the phloroglucol at the same time as, or earlier than, the pentose.

The Conduct of the Pentosans by the Germination of Seeds in Darkness.

In a former paper[1] I gave a preliminary report on this subject. The study of the changes in the amount of vegetable matters

[1] This Journal **15**, 276.

during the germination of seeds in darkness is of fundamental importance for obtaining an insight into the physiological value of these matters. I have therefore continued my investigations in this direction, and the facts which I have pointed out confirm and enlarge my former results.

In my former paper I communicated:

1. That when corn and peas germinate in darkness, the young plants contain more pentosans than the seeds.

2. That the amount of pentosans in the seeds proper decreases.

3. That the young plants of *Trapæolum majus* contain considerably less of the pentosans than the seeds.

4. That it was not decided whether the increase in pentosans in corn and peas was due to a new formation or whether these substances were taken up from the soil. For when peas were grown in asbestos, the young plants contained exactly the same amount of pentosans as the original seeds.

I have in my later experiments always planted the seeds in a medium which did not contain pentosans. In most instances I have taken pumice-stone broken to pieces of about 1 cm. in diameter. I planted about 100 seeds in flat, round dishes of 25 cm. diameter and 7 cm. depth. A hole in the bottom of the dishes allowed the water to flow off. In the experiments in which I have made use of especial solutions for watering, I put the dishes on big funnels and collected the liquid that ran through. This liquid was afterwards made up to the original volume by adding pure water, and was used again for watering. This second solution was somewhat more diluted than the original solution, not only because the plants absorbed a part of the nutritious matter, but also because the pumice-stone retained about 0.5 liter of liquid. Since possibly the same amount of liquid was applied to all the experiments of one group, the solutions used for the different experiments were diluted in about the same proportion and at the same time. The reaction of the solutions was always tested before watering. In all cases, however, it was found to be neutral. I watered every morning and evening. In a few experiments I made water-cultures. I used for these larger flat dishes of 30 cm. diameter and holding about 4.5 liters. Wire-nets with large meshes and thinly covered with paraffin were laid over these dishes. The seeds were put between layers of filter-paper which had been made wet with the solutions to be used. The first roots

were allowed to develop to a length of about 2 cm. The seeds were then fastened in the meshes of the nets so that the roots reached the solution in the dishes but that the seeds proper could not touch it.

I have compared either the seeds with the young plants, or the young plants of two or more experiments made side by side in the same darkened room, with each other. In the latter case all the circumstances but one, the influence of which I wanted to find out, were the same. Experiments where the plants had not developed normally have not been reported. I have made in most instances duplicate analyses. Where only a single analysis has been made, I daresay that the variation from the truth will not have been more than 0.3 per cent. of pentosan; for the largest variation of two duplicate analyses has been 0.5 per cent. My conclusions, however, are based on larger differences than 0.3 per cent. of pentosan, and in far the majority of cases on much larger differences.

I first wished to find out whether the increase of pentosans in the young corn plants could have been due to an absorption out of the soil.

Table I.

250 seeds of corn were laid between layers of wet filtering paper and, after the first root appeared, were transferred into ground glass. They were watered with well-water, of which 1 liter did not contain a trace of pentosans. Since the amount of nutritious matter, especially of potash, in the ash did not seem quite sufficient for the development of the plants, I watered them on the 12th of December with a solution which contained per liter 2 grams potassium chloride and 1 gram secondary sodium phosphate. This application benefited the plants materially. The experiment lasted 18 days (from November 28 to December 16, 1893). 250 plants were harvested.

The seeds contained before the germination 4.87 (4.92; 4.77; 4.91) per cent. of pentosan.

The seeds contained after the germination 7.93 (8.01; 7.85) per cent. of pentosan.

The stems + roots contained 12.51 (12.49; 12.53) per cent. of pentosan.

Before germination. Gram.	After germination. Gram.		Gain or loss. Gram.
1 seed = 0.3483 dry matter.	1 seed	= 0.1998 dry matter.	
	1 stem + root	= 0.0925 "	
	1 plant	= 0.2923 "	—0.0560
1 seed = 0.0170 pentosan.	1 seed	= 0.0158 pentosan.	—0.0012
	1 stem + root	= 0.0116 "	
	1 plant	= 0.0274 "	+0.0104

Pentosans are therefore formed in corn plants which grow in darkness, and the increase of pentosans in young plants is not due to an absorption of these substances from the soil.

This cannot be wondered at, since I have now proved that pentosans are not formed by the assimilation-process, as I have been inclined to believe heretofore. Cross, Bevan and Beadle[1] communicated in a recent article that they have found that by the germination of barley in darkness the amount of pentosans also increases. When we compare the results in Table I with my former results with corn grown in garden earth, we perceive that the increase in pentosans is much larger, and that the amount in the seeds proper has diminished much less (0.0012 gram against 0.0039 gram) in the experiment in ground glass. The latter fact is probably due to the plants grown in garden earth being able to take up nitrogen compounds, as we shall see later on. That the increase of pentosans in the young plants was so much larger than I had found before, I brought into connection with the fact that these plants were further developed. For the loss of dry matter was much larger (0.0560 gram against 0.0278 gram). The experiments reported in Table II confirm this belief; they show that the young corn plants are subject to the same natural law which I found last summer, *viz.* that the amount and the percentage of pentosans increase during the life of the organs of the plants.[2]

Table II.

Seeds of corn were allowed to swell up in a solution which contained per liter 1 gram potassium chloride and 0.67 gram secondary sodium phosphate. They were planted in pumice-stone and watered with well-water. Two experiments were made: the first lasted 15 days (from January 3–18, 1894); the other 24 days (from January 18 to February 11). The temperature of the

[1] Ber. d. chem. Ges. **27**, 1065.

[2] Probably organs where large amounts of reserve substances (not pentosans) are deposited are exempt from this law.

room in both instances was about the same; in both experiments 100 seeds were planted. In the first experiment 93 plants were harvested; in the second, 98. The average seed taken for the first experiment contained 0.3243 gram of dry matter; for the second, 0.3238 gram. I have, however, calculated the results below as if in both instances seeds of 0.3243 gram of dry matter had been taken. This facilitates making the comparisons. I have followed the same practice in the later tables.

The seeds contained before the germination 6.42 per cent. of pentosan.

The plants of experiment 1 contained 10.88 per cent. of pentosan.

The plants of experiment 2 contained 13.00 per cent. of pentosan.

I.

Before the germination. Gram.	After the germination. Gram.	Gain or loss. Gram.
1 seed = 0.3243 dry matter.	1 plant = 0.2586 dry matter.	— 0.0657
1 seed = 0.0208 pentosan.	1 plant = 0.0281 pentosan.	+ 0.0073

II.

1 seed = 0.3243 dry matter.	1 plant = 0.2377 dry matter.	— 0.0866
1 seed = 0.0208 pentosan.	1 plant = 0.0309 pentosan.	+ 0.0101

The experiments with peas formerly reported on were doubtful, for I found that the amount of pentosans increased when the plants were grown in garden-soil, and that the amount remained the same when they were grown in asbestos. That this difference is due to an absorption of pentosans from the soil becomes very doubtful when we look at the results obtained from corn. I have, moreover, found that the amount of pentosans decreases when peas are grown for a longer time in soils which contain much humus and pentosans.

Table III.

Peas were grown in wood-soil for 10 days (from June 24 to July 4, 1893); 125 seeds were planted and 98 plants were harvested. The seeds contained 6.44 per cent. of pentosan; the plants, 8.47 per cent.

Before germination. Gram.	After germination. Gram.	Gain or loss. Gram.
1 seed = 0.2681 dry matter.	1 plant = 0.1746 dry matter.	— 0.0935
1 seed = 0.0173 pentosan.	1 plant = 0.0148 pentosan.	— 0.0025

Table IV.

Peas were grown in garden-soil for 10 days (from June 25 to July 5, 1893); 125 seeds were planted and 108 plants were harvested. The seeds contained 6.62 per cent. of pentosan; the plants, 8.06 per cent.

Before the germination. Gram.	After the germination. Gram.	Gain or loss. Gram.
1 seed = 0.2557 dry matter.	1 plant = 0.1828 dry matter.	— 0.0729
1 seed = 0.0169 pentosan.	1 plant = 0.0147 pentosan.	— 0.0022

To explain these differences I made the following experiments:

Table V.

Peas were grown in pumice-stone. Three experiments of 100 seeds each were started on May 20, 1894. Experiment I was harvested on May 25, experiment II on May 29, and experiment III on June 5. Of experiment I, 83 plants were harvested; of II, 86, and of III, 79 plants. The average seed of I contained 0.2465 gram of dry matter; of II, 0.2488 gram; and of III, 0.2476 gram.

The seeds contained before the germination 6.8 (6.8; 6.8) per cent. of pentosan.

The plants of experiment I contained 7.8 (7.7; 7.9) per cent. of pentosan.

The plants of experiment II contained 8.5 (8.4; 8.6) per cent. of pentosan.

The plants of experiment III contained 8.55 (8.4; 8.7) per cent. of pentosan.

I.

Before the germination. Gram.	After the germination. Gram.	Gain or loss. Gram.
1 seed = 0.2465 dry matter.	1 plant = 0.2244 dry matter.	— 0.0221
1 seed = 0.0168 pentosan.	1 plant = 0.0175 pentosan.	+ 0.0007

II.

1 seed = 0.2465 dry matter.	1 plant = 0.2105 dry matter.	— 0.0360
1 seed = 0.0168 pentosan.	1 plant = 0.0179 pentosan.	+ 0.0011

III.

1 seed = 0.2465 dry matter.	1 plant = 0.1703 dry matter.	— 0.0762
1 seed = 0.0168 pentosan.	1 plant = 0.0146 pentosan.	— 0.0022

The amount of pentosan in peas grown in darkness therefore first increases and afterwards decreases. Since we know that the

pentosans in the seeds of *Trapæolum majus* decrease largely during the germination, it cannot be wondered at that the pentosans in peas also can be converted into other substances. It becomes then, however, doubtful whether the decrease of pentosans in the seed proper is at all due to a removal of pentosans. On the other hand the supposition gains ground that the pentosans in the seeds are converted into other substances, while the pentosans in the young stems and roots are formed from other substances. I have been able to trace only very small amounts of soluble pentosans in germinating seeds,[1] which in connection with other facts makes it appear that the pentosans, as such, are only removed in very small quantities.

We have observed that the amount of pentosans in peas decreases when they grow for a longer period in darkness, and we found that in corn the pentosans increase under these circumstances. This difference is not only due to the pentosans in the pea seeds being more easily converted into other substances, but also to the increase of pentosans in the young pea stems and roots being much less pronounced than in corn plants. The stems + leaves of peas sown on July 25, in the open ground, contained on Aug. 2, 4.8 per cent. of pentosan; on Aug. 7, 4.8 per cent. of pentosan; on Aug. 19, 7.3 per cent of pentosan.

Also in other plants of the leguminous tribe the pentosans seem to increase only slowly.

The stems + leaves of red clover sown on March 31, in the open ground, contained on May 1, 5.6 per cent. of pentosan; on May 30, 7.0 per cent. of pentosan.

In these cases the plants had the benefit of the sunlight, but we shall see later on that this makes little difference in the changes of the amount of pentosans.

After having considered the changes of the pentosans in representatives of the *Graminæ* and *Leguminosæ*, I made one experiment with seeds that contained much fat. These seeds are very poor in pentosans, and if our former deductions are correct we should observe a large increase of pentosans when these seeds germinate in darkness. S. Frankfurt[2] observed an increase of pentosans in the germinating seeds of the sunflower (*Helianthus annuus*), where it was in the ratio of 2.75 : 5.86. I obtained similar results with pumpkin (*Cucurbita Pepo*).

[1] This Journal **15**, 278. [2] Landw. Vers. Stat. **43**, 176.

Table VI.

350 seeds of pumpkin were allowed to swell up in water and were transferred into pumice-stone. The germinative power of the seeds was very small.

They were planted on July 12; 75 plants were harvested from July 20–28. The shelled seeds contained 1.6 (1.6; 1.6) per cent. of pentosan.

The plants contained 4.3 (4.2; 4.4) per cent of pentosan.

Before germination. Gram.	After germination. Gram.	Gain or loss. Gram.
1 seed (shelled) 0.1409 dry matter.	1 plant = 0.1361 dry matter.	− 0.0048
1 seed (shelled) 0.0022 pentosan.	1 plant = 0.0059 pentosan.	+ 0.0037

Before closing this chapter I wish to give a list containing the percentage of pentosan found in the dry matter of different seeds, which may be of use in later investigations:

Corn, 4.65*;[1] 4.07; 3.95; 6.42; 4.87.
Barley, 10.6 [2] (furfurol 5.3).
Pea, 3.81*; 4.27*; 6.8; 6.44.
Acorn (*Quercus falcata*, shelled seeds), 1.34*.
Nasturtium (*Tropæolum majus*, shelled seeds), 11.97*.
Peanut, 2.76*.
Pumpkin, 3.45 (shelled 1.6).
Hemp,[3] 11.02.
Sunflower,[4] shelled seeds, 2.74 (fruits, 12.69).

The Influence of Light.

Since the absence of light might have some influence on the amount of pentosans in the plants, I made the following experiments:

Table VII.

Peas were grown in pumice-stone from June 28 to July 12. Three experiments were started. In experiment I the plants were grown in darkness; in II and III, in light. The experiments stood in the same room. The light was rather diffuse, so that the plants in experiments II and III, though green, had not

[1] Figures marked with * have been obtained by the method of slow distillation and are therefore too low.
[2] Cross, Bevan and Beadle: Ber. d. chem. Ges. **27**, 1064, note.
[3] Frankfurt: Landw. Vers. Stat. **43**, 143.
[4] *Ibid.*

developed normal leaves. It was the intention to allow the plants of experiment III to grow for a longer period, but owing to their abnormal appearance this experiment (III) was discontinued. The plants were watered with a solution which contained per liter 0.5 gram ammonium nitrate, 0.5 gram primary potassium phosphate, 0.25 gram magnesium sulphate, $MgSO_4.7H_2O$, 0.25 gram potassium chloride, 1 gram calcium carbonate.[1] The solution was shaken before it was used. Of experiment I, 62, and of II, 82, plants were harvested.

The seeds of experiment I contained 0.2628 gram of dry matter; those of II contained 0.2636 gram of dry matter.

The seeds before the germination contained 6.45 (6.4; 6.5) per cent. of pentosan.

The plants of experiment I contained 6.95 (6.8; 7.1) per cent. of pentosan.

The plants of experiment II contained 6.65 (6.5; 6.8) per cent. of pentosan.

Before the germination. Gram.	After the germination. Gram.	Gain or loss. Gram.
1 seed = 0.2628 dry matter.	1 plant = 0.1923 dry matter.	— 0.0705
1 seed = 0.0170 pentosan.	1 plant = 0.0134 pentosan.	— 0.0036
	II.	
1 seed = 0.2628 dry matter.	1 plant = 0.1879 dry matter.	— 0.0749
1 seed = 0.0170 pentosan.	1 plant = 0.0125 pentosan.	— 0.0045

Table VIII.

Seeds of corn were grown in pumice-stone from July 18–28. Two experiments of 100 seeds each were started. In experiment I the dish with the plants was put in a box. The plants therefore grew in darkness. The dish with the plants of experiment II was placed on the box. The experiments were placed in the open air under a porch, which shut off the direct rays of the sun. The plants were watered with well-water; on July 25, however, there was applied to the plants of both experiments 0.45 gram potassium chloride and 0.45 gram calcium chloride dissolved in 250 cc. of water. This materially increased their development. The plants of both experiments developed very well; those of II being quite normal. Of experiment I, 95 plants were harvested; of II, 92

[1] This solution was used with a view to experiment III, which, however, failed.

plants. The seeds taken for experiment I contained 0.3485 gram dry matter, those of II, 0.3479 gram.

The seeds contained before the germination 4.4 (4.4; 4.4) per cent. of pentosan.

After the germination the seeds of experiment I contained 10.45 (10.4; 10.5) per cent. of pentosan.

The stems + roots of experiment I contained 12.3 per cent. of pentosan.

The seeds of experiment II contained 10.3 (10.2; 10.4) per cent. of pentosan.

The stems + roots of experiment II contained 12.5 (12.3; 12.7) per cent. of pentosan.

I.

Before germination. Gram.	After germination. Gram.	Gain or loss. Gram.
1 seed = 0.3485 dry matter.	1 seed = 0.1297 dry matter.	
	1 stem + root = 0.1236 "	
	1 plant = 0.2533 "	−0.0952
1 seed = 0.0153 pentosan.	1 seed = 0.0136 pentosan.	−0.0017
	1 stem + root = 0.0152 "	
	1 plant = 0.0288 "	+0.0135

II.

1 seed = 0.3485 dry matter.	1 seed = 0.1342 dry matter.	
	1 stem + root = 0.1282 "	
	1 plant = 0.2624 "	−0.0861
1 seed = 0.0153 pentosan.	1 seed = 0.0138 pentosan.	−0.0015
	1 stem + root = 0.016c "	
	1 plant = 0.0298 "	+0.0145

The experiments with peas (Table VII) have not succeeded very well, for the plants of experiment II did not receive sufficient light to allow them to develop normally. I should have made this experiment over if I had found time. As it is, I believe that in connection with the experiments with corn (Table VIII) I may draw the general conclusion that the influence of the light during the time that plants can grow in darkness is only slight. The composition of the tissue, so far as pentosans are concerned, is little affected.

The Influence of Nitrogen.

I have tried to find out whether the amount of nitrogen compounds at the disposition of the young plants has any influence

on the amount of pentosans which are formed, or which are dissolved during the germination of seeds in darkness. I made these investigations with corn seeds, which contain few nitrogen compounds, and which, therefore, are more apt to be influenced by nitrogen in fertilizers than seeds richer in nitrogen compounds. It had been found by former investigations that the amount of ash constituents in corn seeds is not sufficient to enable them to use their reserve substances to the best advantage. I therefore made two parallel experiments, and watered the first with a solution containing all plant-nutritious matters, and the other with a solution containing all but nitrogen. Nitrogen compounds were applied in the most easily available form, *viz.*, nitrates.

Table IX.

Two experiments of 100 corn seeds each were made in pumice-stone, April 5–28, 1894. They were watered with the following liquids:

	Liquid for Experiment I containing nitrogen.	Liquid for Experiment II without nitrogen.
Nitrogen-free water,	2.25 liters.	2.25 liters.
Sodium nitrate,	2.0 grams.	"
Potassium nitrate,	2.0 "	"
Primary potassium phosphate, KH_2PO_4	1.5 "	1.5 grams.
Magnesium sulphate, $MgSO_4.7H_2O$,	1.0 "	1.0 "
Sodium chloride,	0.5 "	0.5 "
Potassium sulphate,	" "	1.75 "
Calcium carbonate,	1.0 "	1.0 "

Of experiment I, 95 plants were harvested; of II, 92 plants. The seeds for experiment I contained 0.3855 gram of dry matter; those of II, 0.3854 gram. The seeds contained before the germination 3.95 (3.9; 4.0) per cent. of pentosan, 1.70 (1.72; 1.68) per cent. of total nitrogen, and 10.50 (10.63; 10.38) per cent. of albuminoids. The plants of experiment I contained 6.5 (6.7; 6.4; 6.4) per cent. pentosan; 2.30 (2.25; 2.34) per cent. of total nitrogen, and 8.56 (8.56; 8.56) per cent. of albuminoids.

The plants of experiment II contained 8.45 (8.4; 8.5) per cent. of pentosan, 1.98 (2.01; 1.94) per cent. of total nitrogen, and 8.60 (8.25; 8.94) per cent. of albuminoids.

I.

Before germination. Gram.	After germination. Gram.	Gain or loss. Gram.
1 seed = 0.3855 dry matter.	1 plant = 0.3380 dry matter.	−0.0475
1 seed = 0.0152 pentosan.	1 plant = 0.0220 pentosan.	+0.0068
1 seed = 0.0066 total nitrogen.	1 plant = 0.0078 total nitrogen.	+0.0012
1 seed = 0.0405 albuminoids.	1 plant = 0.0289 albuminoids.	−0.0116

II.

1 seed = 0.3855 dry matter.	1 plant = 0.3275 dry matter.	−0.0580
1 seed = 0.0152 pentosan.	1 plant = 0.0277 pentosan.	+0.0125
1 seed = 0.0066 total nitrogen.	1 plant = 0.0065 total nitrogen.	−0.0001
1 seed = 0.0405 albuminoids.	1 plant = 0.0282 albuminoids.	−0.0123

We observe that the young plants of experiment I have taken up considerable quantities of nitrates. The percentage of albuminoid in the plants of both experiments was, however, about the same. The plants to which nitrates had been applied contained considerably less pentosans than the others. But this might be due to another reason than the influence of the nitrogen compounds. For these plants probably, owing to the higher concentration of the solution, had lost less in dry matter. This indicates that they were not as far developed, and the amount of pentosans in corn increases when the development of the plant advances.

Therefore new experiments were started in which I wanted to find out at the same time whether the pentosans will decrease in young corn plants if large amounts of nitrates are applied, and if the plants are allowed to develop as far as possible. In this case sodium sulphate was added to the nitrogen-free solution in order to make up for the smaller concentration caused by the absence of nitrates.

Table X.

Four experiments with corn in pumice-stone were started on June 9. In experiments I and III the plants received nitrogen in fertilizers, in experiments II and IV they did not. The solutions for watering contained:

	I and III.	II and IV.
Nitrogen-free water,	2.25 liters.	2.25 liters.
Ammonium nitrate,	1.5 grams.	..
Primary potassium phosphate,	1.0 "	1.0 gram.
Magnesium sulphate, $MgSO_4.7H_2O$,	0.5 "	0.5 "
Potassium chloride,	0.5 "	0.5 "
Sodium sulphate,	..	1.75 "
Calcium carbonate,	2.0 "	2.0 "

After 5 days there was added to the solution containing nitrogen 1 gram of ammonium nitrate, and to the nitrogen-free solution 2.25 grams of sodium sulphate.

Experiments I and II were harvested on June 19, experiments III and IV on June 24. The plants of experiment III were dying when harvested; their roots were dead and so were the underparts of the stems. The leaves, however, were still quite fresh. The water which had run through the pumice-stone of this experiment had dissolved substances from the roots, for it had become slightly colored and had the odor of the crushed plants.

Of experiment I 100 plants were harvested, of II, 99 plants, of III, 83 plants, and of IV, 93 plants.

The seeds of experiment I contained 0.2789 gram of dry matter; those of II, 0.2802 gram; those of III, 0.2802 gram; and those of IV, 0.2823 gram.

The seeds contained before the germination 4.07 (4.3; 3.8; 4.1) per cent. of pentosan.

The plants of experiment I contained 12.5 (12.5; 12.5) per cent. of pentosan.

The plants of experiment II contained 13.45 (13.3; 13.6) per cent of pentosan.

The plants of experiment III contained 14.4 per cent. of pentosan.

The plants of experiment IV contained 14.75 (14.7; 14.8) per cent. of pentosan.

I.

Before germination. Gram.	After germination. Gram.	Gain or loss. Gram.
1 seed = 0.2789 dry matter.	1 plant = 0.1862 dry matter.	−0.0927
1 seed = 0.0114 pentosan.	1 plant = 0.0233 pentosan.	+0.0119

II.

1 seed = 0.2789 dry matter.	1 plant = 0.1931 dry matter.	−0.0858
1 seed = 0.0114 pentosan.	1 plant = 0.0260 pentosan.	+0.0146

III.

1 seed = 0.2789 dry matter.	1 plant = 0.1608 dry matter.	−0.1181
1 seed = 0.0114 pentosan.	1 plant = 0.0232 pentosan.	+0.0118

IV.

1 seed = 0.2789 dry matter.	1 plant = 0.1914 dry matter.	−0.0875
1 seed = 0.0114 pentosan.	1 plant = 0.0282 pentosan.	+0.0168

The loss in dry matter of the plants of experiment I was larger than that of the plants of II. The former were practically

exhausted. Still they contained less pentosan than the plants of experiment II. The plants of experiment III were partly dead. They did not contain more pentosan than those of I, for they seemed not to have developed any further. They contained, however, much less dry matter, which probably had been washed out of the dead parts. The plants of experiment IV were farther developed than those of II, but not even quite as far as those of I. They contained more pentosan than those of II, and considerably more than those of I and III. These results fairly prove that the nitrogen compounds tend to decrease the formation of pentosans, or to facilitate their decomposition. The amount of pentosans, however, does not decrease in corn plants even when nitrogen compounds are liberally applied. They even do not decrease after parts of the plants have died off and decomposition has set in. This latter fact cannot be wondered at, for we know that the pentosans of dead corn leaves are also much less readily decomposed and washed out of the leaves than other vegetable matters.

It was further of interest to find out whether the nitrogen compounds only decrease the formation of pentosans in the stems and roots or whether they also facilitate the decomposition of the pentosans of the seeds. The experiments reported in Tables XI and XII prove that they do both.

Table XI.

Two experiments of 100 corn seeds each were started on July 31. The seeds were put between layers of wet filtering paper, and after they had developed the first root, were suspended in wire-netting over flat dishes so that the roots entered into the following solutions:

	Solution containing nitrogen. Experiment I.	Nitrogen-free solution. Experiment II.
Nitrogen-free water,	4.0 liters.	4.0 liters.
Ammonium nitrate,	0.5 gram.	..
Potassium nitrate,	1.5 "	..
Primary potassium phosphate,	1.0 "	1.0 gram.
Potassium chloride,	0.25 "	1.35 "
Magnesium sulphate,	0.5 "	0.5 "
Calcium carbonate,	1.0 "	1.0 "
Sodium sulphate,	..	0.9 "

On August 4 there was added 0.5 gram of ammonium nitrate to solution I. The volume of the solution was kept stationary by

adding nitrogen-free water. Every day 2 liters of air free of nitrogen compounds were driven through each of the solutions.

Of experiment I 93 plants were harvested on August 9 (9 days). Experiment II was harvested 12 hours later, on the morning of August 10; it yielded 94 plants. The seeds of experiment I contained 0.3499 gram of dry matter; those of II, 0.3491 gram. The seeds before the germination contained 4.4 (4.4; 4.4) per cent. of pentosan. The seeds of experiment I contained after the germination 6.0 (6.1; 5.9) per cent., and the stems + roots 9.8 per cent. The seeds of experiment II contained after the germination 5.65 (5.6; 5.7) per cent., and the plants 11.8 per cent. of pentosan.

I.

Before germination. Gram.	After germination. Gram.		Gain or loss. Gram.
1 seed = 0.3499 dry matter.	1 seed	= 0.2222 dry matter.	..
	1 stem + root	= 0.0762 "	..
	1 plant	= 0.2984 "	−0.0515
1 seed = 0.0154 pentosan.	1 seed	= 0.0133 pentosan.	−0.0021
	1 stem + root	= 0.0075 "	..
	1 plant	= 0.0208 "	+0.0054

II.

1 seed = 0.3499 dry matter.	1 seed	= 0.2515 dry matter.	..
	1 stem + root	= 0.0607 "	..
	1 plant	= 0.3122 "	−0.0377
1 seed = 0.0154 pentosan.	1 seed	= 0.0142 pentosan.	−0.0012
	1 stem + root	= 0.0072 "	..
	1 plant	= 0.0214 "	+0.0060

Table XII.

Two experiments of 110 corn seeds each were started on August 2. The plants, which grew in pumice-stone, were watered with:

	Solution containing nitrogen. Experiment I.	Nitrogen-free solution. Experiment II.
Nitrogen-free water,	2.25 liters.	2.25 liters.
Ammonium nitrate,	1.5 gram.	..
Primary potassium phosphate,	1.0 "	1.0 gram.
Potassium chloride,	0.5 "	0.5 "
Magnesium sulphate,	0.5 "	0.5 "
Calcium carbonate,	0.5 "	0.5 "
Sodium sulphate,	..	1.75 "

On August 8, 1 gram of ammonium nitrate was added to solution I. Of experiment I, 102 plants were harvested on August 13

(11 days); of II, 91 plants were harvested on the morning of August 15 (36 hours later). The seeds for experiment I contained 0.3328 gram of dry matter; those of II, 0.3315 gram.

The seeds contained before the germination 4.4 (4.4; 4.4) per cent. of pentosan.

The seeds of I contained after the germination 10.15 (10.4; 9.9) per cent. of pentosan.

The stems + roots of I contained 10.55 (10.5; 10.6) per cent. of pentosan.

The seeds of II contained 13.8 (13.7; 13.9) per cent. of pentosan.

The stems + roots of II contained 13.6 (13.5; 13.7) per cent. of pentosan.

The stem + roots of I contained 15.92 per cent. of albuminoids.

The stem + roots of II contained 11.69 (11.63; 11.75) per cent. of albuminoids.

I.

Before germination. Gram.	After germination. Gram.	Gain or loss. Gram.
1 seed = 0.3328 dry matter.	1 seed = 0.0939 dry matter.	..
	1 stem + root = 0.1440 "	..
	1 plant = 0.2379 "	—0.0949
1 seed = 0.0146 pentosan.	1 seed = 0.0095 pentosan.	—0.0051
	1 stem + root = 0.0152 "	..
	1 plant = 0.0247 "	+0.0101
	1 stem + root = 0.0229 albuminoids.	..

II.

1 seed = 0.3328 dry matter.	1 seed = 0.0959 dry matter.	..
	1 stem + root = 0.1350 "	..
	1 plant = 0.2309 "	—0.1019
1 seed = 0.0146 pentosan.	1 seed = 0.0132 pentosan.	—0.0014
	1 stem + root = 0.0184 "	..
	1 plant = 0.0316 "	+0.0170
	1 stem + root = 0.0158 albuminoids.	..

The plants of experiment I (Table XI) have been much further developed than those of experiment II; hence the results are less obvious. The results reported in Table XII are very convincing. Though the plants of experiment I were a little less developed than those of II, this difference is only small, while the difference in the amount of pentosans, both in the stems + roots, and in the seeds, is very pronounced. The stems + roots of experiment I (Table XII) also contain considerably more albuminous matters than those of experiment II.

Résumé.

1. Pentosans are present in the stems which are developed from barley seeds that germinate in darkness. There is no reason to assume in these stems other substances which yield furfurol or so-called oxycelluloses. Far the larger part of the furfurol-yielding compounds in these stems is, moreover, soluble in strongly diluted acids and alkalies, and therefore does not belong to the celluloses proper.

2. The amount of pentosans increases in corn which is allowed to germinate in darkness, and this increase is not due to an absorption of pentosans from the soil, but to a formation of pentosans from other substances. For such an increase of pentosans takes place when the seeds are planted in pumice-stone which does not contain pentosans.

3. The more the development of the young plants is advanced, the more pentosans do they contain.

4. When peas are allowed to germinate in darkness, the amount of pentosans first increases and then decreases.

5. The facts lead to the conclusion that the pentosans in the seeds are decomposed, and those in the stems and roots are newly formed, but that the transportation of pentosans as such is only of subordinate importance.

6. Seeds which contain much fat contain only a small amount of pentosans, but this increases materially during the germination in darkness.

7. The absence of light has only little, if any, influence on the conduct of the pentosans during the short time that seeds can develop in darkness.

8. When besides all other nutritious matters, nitrates are applied to seeds which are germinating in darkness, the pentosans of the seeds are more readily decomposed, and less pentosan is formed in the young stems + roots. The latter, on the other hand, contain more albuminous matter.

II.—The Formation of Pentosans in Plants.

In my paper on "Soluble pentoses in plants"[1] I put forward the following general proposition:

[1] This Journal **15**, 21.

"Pentoses are either formed along with hexoses by the assimilation process, or the plants have the power to form pentoses from hexoses."

In my subsequent investigations I have shown that pentoses are not formed by the assimilation process.[1] Hence pentoses are elaborated from hexoses. In the first part of this paper it is, moreover, shown that the pentoses increase to a very great extent in corn which is allowed to germinate in darkness. I shall now make an attempt to solve the question, in what manner the pentoses are formed from hexoses, and shall therefore make use of the chemical and physiological facts which have come to my knowledge. I am sorry to acknowledge, however, that my solution of this problem must still be regarded as an hypothesis.

By hydrolysis of the pentosans two pentoses have been found to result, *viz.*, *l*-xylose and *l*-arabinose.

Xylans (pentosans which yield xylose) are in almost every instance intermixed with, or chemically united with glucosans. Wood-gum, for example, is always found beside glucose-cellulose. In several celluloses, xylose molecules are so strongly united with glucose molecules that they cannot be separated without breaking up the cellulose.[2]

Arabans (pentosans which yield arabinose) are in most instances found beside galactans—in fact so frequently that arabinose and galactose were formerly often confounded. They are beside each other in arabinic acid,[3] in the gums that are exuded from the barks of the cherry[4] and the peach trees,[5] in gum tragacanth,[6] in coffee-beans,[7] and in the paragalactan which is found in seeds of many leguminoses.[8] Galactose molecules were never found in celluloses,[9] and neither were arabinose molecules.

It is true that in some exceptional cases xylose was found beside little or no glucose, and arabinose without galactose. Thus Stone[10] found a gum in the fruits of *Gymnocladus Canadensis*

[1] J. Am. Chem. Soc. **16**, 618.

[2] E. Schulze: Ber. d. chem. Ges. **24**, 2277; Winterstein: Ztschr. physiol. Chem. **17**, 382; Tollens and Schulze: Ann. Chem. (Liebig) **271**, 55.

[3] Tollens: Kohlehydrate, 214.

[4] *Loc. cit.*

[5] Stone: This Journal **12**, 435.

[6] Tollens: Kohlehydrate, 217.

[7] E. Elwell: This Journal **14**, 473.

[8] E. Schulze: Landw. Vers. Stat. **41**, 223; Ztschr. physiol. Chem. **14**, 227.

[9] Ber. d. chem. Ges. **24**, 2281.

[10] This Journal **15**, 660.

which is probably composed of glucose and arabinose molecules. Winterstein[1] found in amyloid galactose, xylose and but little glucose.

E. Schulze and Steiger[2] and C. Schulze and Tollens[3] found in bran of wheat and rye a little arabinose along with xylose and glucose, but they did not find galactose.

If we compare the formulæ proposed by E. Fischer[4] for *d*-glucose and *l*-xylose, and those for *d*-galactose[5] and *l*-arabinose, it must strike us that a great similarity exists:

$$\begin{array}{c} \text{H H OH H} \\ \text{CH}_2\text{(OH).C . C . C . C .C.OH, } d\text{-glucose;} \\ \text{OH OH H OH} \end{array}$$

$$\begin{array}{c} \text{H OH H} \\ \text{CH}_2\text{(OH).C . C . C.C.OH, } l\text{-xylose;} \\ \text{OH H OH} \end{array}$$

$$\begin{array}{c} \text{H OH OH H} \\ \text{CH}_2\text{(OH).C . C . C . C.C.OH, } d\text{-galactose;} \\ \text{OH H H OH} \end{array}$$

$$\begin{array}{c} \text{OH OH H} \\ \text{CH}_2\text{(OH).C . C . C .C.OH, } l\text{-arabinose.} \\ \text{H H OH} \end{array}$$

We observe that *l*-xylose would result if the alcohol group at the end of the *d*-glucose molecule was eliminated. *l*-Arabinose would in the same manner result from *d*-galactose. This would be the case if the alcohol group at the end of the *d*-hexose molecule were oxidized to carboxyl and then carbonic acid split off. Intermediate products between the *d*-hexoses and *l*-pentoses would then be: firstly, compounds with two aldehyde groups and isomeric in structure with glucosone; secondly, glucuronic acid (from glucose) or a stereo-isomeric acid (from galactose). Such an oxidation could take place only if the original aldehyde

[1] Ber. d. chem. Ges. **25**, 1237.
[2] Ann. Chem. (Liebig) **271**, 55.
[3] *Ibid.* **23**, 3110.
[4] Ber. d. chem. Ges. **24**, 2685.
[5] *Ibid.* **27**, 385.

group of the hexose was bound to other groups and thereby preserved from further oxidation. E. Fischer accepts this also in order to explain the formation of glucuronic acid from glucose in the animal body.[1] It is remarkable that the pentose molecules in plants are almost always united to big complex molecules in which all or at least the majority of the aldehyde groups are bound by condensation. I could only trace very small amounts of soluble pentosans which are readily diffusible through membranes and which may be simple pentoses.[2]

These soluble pentosans may, moreover, be formed from insoluble and complex pentosans.[3] The very small amount of soluble pentosans also indicates that the pentosans are formed at the places where we find them.

Carbonic acid is readily split off from glucuronic acid, for this acid yields almost as much furfurol as the pentoses when it is heated with diluted mineral acids.[4]

I wish now to put forward the following hypothesis: Pentose molecules are formed in complex molecules of hexosans (celluloses and hemi-celluloses) in which a part or all of the aldehyde groups have been bound by cendensation and are thereby preserved from further oxidation. Pentose molecules are formed from hexoses by the alcohol group at the end of the hexose molecule being oxidized to carboxyl and carbonic acid being split off.

I wish to leave it undecided whether there are in some pentosans molecules to which the aldehyde or carboxyl groups still adhere. This is, however, not impossible. Such pentosans should contain more oxygen. Molecules of the formula $C_6H_8O_6$, and which would be formed by the condensation of glucuronic acid, should contain 40.91 per cent. of carbon, while molecules formed by the condensation of hexoses ($C_6H_{10}O_5$) contain 44.44 per cent., and those formed of pentoses ($C_5H_8O_4$) 45.45 per cent. Cross, Bevan and Beadle[5] found 42.4 and 41.8 per cent. of carbon in the cellulose of graminæ. The percentage of hydrogen which they found was also less than compounds of the formulæ $C_6H_{10}O_6$ or $C_5H_8O_4$ would require. This cellulose yields large amounts of furfurol, and contains groups of molecules which show the pentose reaction with phloroglucol.[6] But pentoses and glucuronic acid

[1] Ber. d. chem. Ges. **24**, 524.
[2] This Journal **15**, 21.
[3] *Ibid.* **15**, 276.
[4] Ber. d. chem. Ges. **25**, 2569.
[5] *Ibid.* **27**, 1063.
[6] E. Schulze: *Ibid.* **24**, 2283.

both show these reactions. I shall endeavor to obtain additional support for my hypothesis, but I am aware that it alone can never entirely explain the formation of pentosans in plants, for this formation takes place only in living cells.[1]

III.—Pentosans in Pine Wood.

Some time ago I found that the unfinished oak wood contains less pentosans than the wood of which the formation is accomplished. According to Wieler,[2] unfinished wood of *Pinus sylvestris* contains 14–15 per cent. of wood-gum. Since I found no more than 10 per cent. of pentosan in pine wood, it seems as if either the pentosans decrease instead of increasing by the formation of this wood, or that the wood-gum of Wieler does contain other substances than pentosans. I have not found time to investigate this subject more fully, but I proved that in pine wood also the amount of pentosans increases during its formation. A pine, *Pinus taeda*, of about 40 years was cut down in the commencement of June and was investigated immediately afterwards. The wood contained, unfinished young wood, 7.65 (7.5; 7.8) per cent. of pentosan; mature wood of 10 and more years old, 9.85 (9.8; 9.9) per cent. of pentosan.

Johns Hopkins University.

ON CHEMICAL EQUILIBRIA AS TEMPERATURE-FUNCTIONS.

By J. E. Trevor and F. L. Kortright.

The consideration that the only things of which we can take direct cognizance are manifestations of energy, and that the total energy of an isolated system remains constant in amount or, in other words, subsists, leads at once to the idea of the substantiality of energy and to the conception that all natural processes are in their ultimate nature energy transformations. This makes the

[1] See my investigation of the wood-formation: This Journal **16**, 218.
[2] Landw. Vers. Stat. **32**, 307.

equilibrium of any material system subject to the condition that a possible variation of any one of the forms of energy which it includes must be exactly compensated by the corresponding variation of the forms correlated with this one; the criterion of equilibrium being that the algebraic sum of the energy changes involved in a virtual displacement of the equilibrium must vanish. Denoting any energy form by E, this condition is expressed analytically by

$$\Sigma \delta E = 0, \qquad (1)$$

the summation being taken over all the correlated energies of the system. The proposition in this general form is known as the Principle of Virtual Energies; its first clear and comprehensive statement is due to Ostwald.[1] The resolution of an energy-form into its intensity-factor I, the quantity which measures its tendency for transference, and the capacity-factor C, the quotient of the energy by its intensity, shows that in general the above equation is to be employed in the more special form,

$$\Sigma C dI = 0, \qquad (2)$$

to represent the equilibrium of the virtual energy-changes about a displaceable equilibrium.

When this criterion is applied to the equilibrium between heat Q and work W, it furnishes the fundamental differential equation for the equilibria of thermodynamics, in the form,

$$\Sigma dW = \frac{Q}{T} dT, \qquad (3)$$

T representing the absolute or energetic temperature of the heat quantity Q. This equation contains the theory of all displaceable chemical equilibria, because such equilibria always involve heat and some one or more entirely convertible forms of energy; for isothermal equilibria it becomes, of course,

$$\Sigma dW = 0, \qquad (4)$$

the Principle of Virtual Work.

In all customarily considered types of cases the chemical equilibria which appear involve thermal and volume energies, and the influence of temperature-changes upon them must be regarded as displacements due to the addition of heat of an increased intensity

[1] Ztschr. phys. Chem. **10**, 363 (1892).

(temperature), or the reverse. There are two cases to be considered, the Complete and the Incomplete Equilibria of the Phase Rule.

I. *Complete Equilibria.*—When n substances compose a chemical system of $n+1$ heterogeneous phases, one of which is vapor, the equilibrium is a function of but one independent variable, and its equilibrium-equation, the differential equation of the "Boundary curve," is

$$+\frac{\rho}{T}.dT=vdp, \tag{5}$$

or

$$RTd\log_e p-\frac{\rho_T}{T}.dT=0.$$

Here p is the equilibrium-pressure at the temperature T, ρ is the total molecular heat of change, *i. e.* the heat Q absorbed at constant volume plus RT the volume energy (normally) obtained, and R is the constant of the gas-equation $pv=RT$. To get rid of the volume energy term we subtract $\frac{d\log_e T}{dT}=\frac{1}{T}$ from both members, and there results

$$RT\partial\log_e K-\frac{Q_T}{T}.\partial T=0, \tag{5a}$$

$\log_e K$ being the characteristic constant of the reaction-isotherm. For, $\frac{p}{T}=c$, the molecular concentration of the saturated vapor, and is therefore proportional to K. The relation (5*a*) is the famous law of van't Hoff[1] for the displacement of a movable chemical equilibrium.

II. *Incomplete Equilibria.*—When n independent components make up a system of less than $n+1$ heterogeneous phases the isothermal equilibrium of the system depends, to a greater or less degree, upon the relative concentrations of its components, and the balance existing between the respective volume-energies of the latter will be disturbed by a possible addition of heat. The sum of the virtual changes then becomes, for a final equilibrium,

$$(\Sigma vdp-\Sigma VdP)-\frac{Q_T}{T}.dT=0, \tag{6}$$

P, V, p and v representing the partial pressures and molecular volumes of the original reacting substances and of those produced

[1] Handlingar der Stockholmer Akad. 21, No. 17, p. 18 (1886).

by the reaction, respectively. Q_T is, as before, the molecular heat of the reaction considered as occurring at constant volume and at the equilibrium-temperature T.[1] It has been shown elsewhere[2] that the bracketed member of this equation becomes $RT\partial \log_e K$ on the elimination of the pressures, so we have

$$RT\partial \log_e K - \frac{Q_T}{T} . \partial T = 0, \qquad (6a)$$

identical with (5*a*) and representing, therefore, the effect of changes of temperature in displacing *all* types of chemical equilibrium under discussion. This remarkable equation is usually written in the form

$$\frac{\partial \log_e K}{\partial T} = \frac{Q_T}{RT^2}; \qquad (7)$$

by writing the differential coefficient as $\frac{1}{K} \cdot \frac{\partial K}{\partial T}$, *i. e.* the percentage rate of change of the equilibrium-constant per degree, its meaning is at once seen to be that the temperature-coefficient of reaction depends upon the heat of reaction and is a function of the absolute temperature. The qualitative result, that a rise of temperature will displace a chemical equilibrium in the direction in which the reaction absorbs heat, is familiar to every one.

To find, from the *rate* $\frac{1}{RT} \cdot \frac{Q}{T}$ with which an equilibrium changes with the temperature, the amount of change corresponding to a finite interval of temperature, the expression (7) must be integrated between the temperature limits; this is not a simple matter, for the reason that Q depends upon the specific heats of the reacting substances and the specific heats are unknown functions of the temperature. In the customary applications which are made to illustrate van't Hoff's law, the heat of reaction is

[1] In the case of the virtual displacement in a rigid shell,

$$\Sigma v d\rho - \Sigma V dP - \frac{Q_T}{T} . dT = 0,$$

the equilibrium is between the volume-energies on each side, and their displacements mutually cancel—those in one sense are exactly balanced by the corresponding ones in the other. In the case of a vaporization, or the like,

$$v d\rho - \frac{\rho_T}{T} . dT = 0,$$

the change of volume-energy is, on the contrary, not counterbalanced, and ρ is therefore the heat of reaction under constant pressure, *i. e.*, $\rho_T = Q_T + RT$.

[2] Trevor: J. Am. Chem. Soc. **15**, 14 (1893).

assumed to be constant over a very small range of temperatures;[1] but this procedure greatly restricts such applications and in general leaves much to be desired, so that in presenting the matter in the course of the regular lectures upon Physical Chemistry given in Cornell University a more rigid integration has been employed, and with success.

The heat of reaction Q_T absorbed at the absolute temperature T, being the energy-difference of the reacting systems, is that, Q_0, at some arbitrarily selected standard temperature T_0 increased for each degree by the excess of the total molecular heat of the system II which is produced by the reaction over that of the original system I. In symbols

$$Q_T = Q_0 + \left(\frac{\partial Q_{II}}{\partial T} - \frac{\partial Q_I}{\partial T}\right)(T - T_0), \qquad (8)$$

i. e.,
$$Q_T = Q_0 + (c_{II} - c_I)(T - T_0). \qquad (8a)$$

With this value of Q_T, van't Hoff's equation becomes

$$\partial \log_e K = \frac{Q_0}{R} \cdot T^{-2} \partial T + \frac{c_{II} - c_I}{R}(T - T_0) \cdot T^{-2} \partial T, \quad (9)$$

or

$$\int_{K_1}^{K_2} \partial \log_e K = \frac{Q_0 - T_0 \cdot \Delta c}{R} \int_{T_1}^{T_2} T^{-2} \cdot \partial T + \frac{\Delta c}{R} \int_{T_1}^{T_2} T^{-1} \partial T, \quad (10)$$

making the permissible assumption that the difference Δc of the specific heats is constant between wide temperature-limits. The integration gives

$$\log_e \frac{K_2}{K_1} = \frac{Q_0 - T_0 \cdot \Delta c}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{\Delta c}{R} \log_e \frac{T_2}{T_1}, \quad (11)$$

or, for the heat of reaction,

$$Q_0 = \frac{T_1 T_2}{T_2 - T_1}\left(R \log_e \frac{K_2}{K_1} - \Delta c \log_e \frac{T_2}{T_1}\right) + T_0 \cdot \Delta c. \quad (11a)$$

To illustrate the application of this relation let us consider the simplest case conceivable, the vaporization-equilibrium of water, and calculate the heat of vaporization from the vapor-pressure curve. For the equilibrium

$$Liquid \gtrless Vapor,$$

the reaction-isotherm is

$$K.C = c,$$

[1] See, for example, van't Hoff: Études, 128–139; and Nernst: Theor. Chem. 514–521.

C and c representing the respective molecular concentrations of the two phases, and hence

$$K = \frac{1}{C} \cdot c = const \times \frac{p}{T}$$

from the relation $p = cRT$ obtaining for the vapor. We have therefore

$$\log_e \frac{K_2}{K_1} = \log_e \frac{\frac{p_2}{T_2}}{\frac{p_1}{T_1}}.$$

The formula (11*a*) being applicable to any temperature-interval, we may select widely separated temperatures, say 50° and 100° C., and thus introduce large and accurately known vapor-pressures. The most accurate available data for the vapor-pressures and the specific heats at constant volume are:

$T_1 = 323°$	$T_2 = 373°$
$p_1 = 91.98$ *mm. Hg*	$p_2 = 760$[1]
$c_I = 18 \times 1.02$ *cal*[2]	$c_{II} = 18 \times 0.47$[3]
$\Delta c = -9.90$ *cal.*	

These values substituted in (11*a*) give $Q_0 = 10201$ *cal* as the heat of vaporization of water at 0° C., reduced to constant volume. Addition of the volume-energy of the mol[4] of expanding vapor,

$$pv = 2T = 2 \times 273 = 546 \text{ cal}, \qquad \text{gives}$$
$$\rho_0 = 10201 + 546 = 10747 \text{ cal},$$

while the two experimental determinations which have been made in recent years are (when expressed in the unit employed above, the zero-degree calorie)

Dieterici[5]	10742 *cal*
Hartog and Harker[6]	10722 " .

[1] Regnault.

[2] The mean of the best determinations near 75° C., *i. e.* of the nine values cited in Landolt and Börnstein's "Tabellen," 133–134, with the exception of the first two, which are obviously faulty.

[3] Given by Gray as 0.3787 at constant pressure at 100°–125°, which is lower than that found by Regnault for higher temperatures, so for 50°–100° we round off the value to 0.37, and convert to the condition of constant volume by the accepted ratio $k = 1.274$ at 78°.

[4] For the employment of this term to express the gram-molecular weight, see Ostwald: Ztschr. phys. Chem. **13**, 375 (1894).

[5] Ann. der Phys. Wied. **37**, 494 (1889).

[6] Abstracted in Beibl. zu den Ann. der Phys. Wied. **18**, 902 (1894).

The theoretical result is thus seen to differ from the average of the best experimental ones by only fifteen gram-calories, or less than two-tenths of one per cent. (0.14 per cent.), an agreement which very satisfactorily speaks for the correctness of the theory. No such result can possibly be reached on the assumption of a heat of change which is independent of the temperature.

One other curious relation may be worthy of mention in this connection; since the displacement of an equilibrium is determined by the temperature-change, the heat of reaction and the difference of the molecular heats of the reacting systems, it follows that this difference of the molecular heats is a function of the other quantities named. Equation (11), in fact, when solved for Δc gives

$$\Delta c = \frac{T_1 T_2 R \log_e \frac{K_2}{K_1} - Q_0 (T_2 - T_1)}{T_1 T_2 \log_e \frac{T_2}{T_1} - T_0 (T_2 - T_1)} \qquad (12)$$

which permits a calculation of the difference of the total molecular heats (considered as independent of the temperature) from a temperature change, the corresponding displacement of the equilibrium, and the heat of the reaction. The relation is entirely general.

It may, further, be worth while to emphasize that in an entirely strict theory, the dependence of the molecular heats upon the temperature may not be omitted from consideration. When this is considered, the approximate form

$$Q_T = Q_0 + (c_{II} - c_I)(T - T_0)$$

becomes the exact one

$$Q_T = Q_0 + \int_0^T \left(\frac{\partial Q_{II}}{\partial T} - \frac{\partial Q_I}{\partial T} \right) . dT,$$

in which $\frac{\partial Q_I}{\partial T} = \varphi_I(T)$ represents the molecular heat of the initial system, and $\frac{\partial Q_{II}}{\partial T} = \varphi_{II}(T)$ that of the system produced. Van't Hoff's law becomes then

$$\frac{\partial \log_e K}{\partial T} = \frac{Q_0}{R} \cdot \frac{1}{T^2} + \frac{1}{R} \cdot \frac{\int_0^T \left(\frac{\partial Q_{II}}{\partial T} - \frac{\partial Q_I}{\partial T} \right) . dT}{T^2},$$

and its integral

$$\log_e K = -\frac{Q_0}{R} \cdot \frac{1}{T} + \frac{1}{R} \int \frac{\int_0^T [\varphi_{II}(T) - \varphi_I(T)] dT}{T^2} \partial T.$$

This function consists of the familiar term $-\frac{Q_0}{RT}$ plus a correction accounting for the gradual variation of the molecular heats with changing temperature. In attempting to complete the integration we run against one of the most fundamental problems of physical science, the relation between specific heat and temperature.

We may now pass with profit to a discussion of the temperature-displacement of the equilibrium in a system containing two convertible components, a process more peculiarly chemical in its nature than the displacement of the vaporization-equilibrium of water. Such a process is involved in the variable dissociation of carbon dioxide, a matter which has been made the subject of a noteworthy paper by Le Chatelier.[1] The dissociation of carbon dioxide is the reversal, at higher temperatures, of the combustion of carbon monoxide, and takes place according to the equation

$$2CO_2 \rightleftarrows 2CO + O_2.$$

The law of the displacement, by a temperature-change, of the equilibrium thus represented is the relation above derived,

$$\log_{10}\frac{K_2}{K_1} = \frac{1}{2 \times 2.3}\int_{T_1}^{T_2}\frac{Q}{T^2}\cdot\partial T, \qquad (13)$$

in which $\log_e\left(\frac{K_2}{K_1}\right)$ is the increment of the characteristic constant of the logarithmized reaction-isotherm over the temperature-interval $T_2 - T_1$.

In order to be able to effect the indicated integration, the heat of the reaction—the Heat of Dissociation of carbon dioxide—must first be determined as a function of the temperature; we shall then be in position, from any known state of the equilibrium to calculate those at all accessible temperatures and pressures.

The heat of dissociation of one mol of carbon dioxide at 18° C., the negative value of the heat of combustion of carbon monoxide, is, according to the best determinations, 68170 *cal*,[2] at constant pressure, or, at constant volume, by subtracting the energy RT due to the change of volume and doubling the result for the two mols of carbon dioxide concerned,

$$Q_{291} = 2.(68170 - 2 \times 291);$$

[1] Ztschr. phys. Chem. **2**, 782 (1888). [2] Berthelot: Ann. chim. phys. (5) **13**, 11 (1878).

in general, therefore, Q at the absolute temperature T is given by the expression

$$Q_T = 2.(68170 - 2 \times 291) + \Delta c(T - 291), \qquad (14)$$

in which Δc is the difference of the total molecular heats.[1] This difference, for the reaction

$$2CO + O_2 = 2CO_2$$

is $$\Delta c = 2c_{CO} + c_{O_2} - 2c_{CO_2}$$

or $$\Delta c = \overbrace{2 \times 6.79} + \overbrace{6.96} - \overbrace{2.(6.8 + 0.0072\,T)}$$

at constant pressure;[2] at constant volume it becomes

$$\Delta c = \frac{2 \times 6.79}{1.4} + \frac{6.96}{1.41} - \frac{2.(6.8 + 0.0072\,T)}{1.3},$$

adopting the ratios of the specific heats as given in the new edition of Landolt and Börnstein's tables, p. 340. It is to be noted that the specific heats of carbon monoxide and of oxygen are independent of the temperature within wide limits. Condensing the above expression,

$$\Delta c = 4.17 - 0.011077\,T. \qquad (15)$$

When this value is substituted in the formula (14) for Q_T, and reduced, we obtain

$$Q_T = 133963 + 7.393407\,T - 0.011077\,T^2, \qquad (16)$$

which is the function $Q_T = \varphi(T)$ required.

It may be remarked in passing that in Le Chatelier's paper, which is cited above, the difference of the heat-capacities of the opposed systems of the reaction is erroneously represented by

$$1c_{CO} + 1c_{O_2} - 1c_{CO_2},$$

[1] In the complete dissociation under constant pressure the volume is increased in the ratio 3 : 2, the work $pv = 2T$, being therefore done per two mols of the dioxide. With one mol but half this work is to be subtracted, so that the expression preceding (14) should read

$$Q_{291} = 2\,(68170 - 291).$$

The oversight in the text involves an unimportant error in Q of less than 0.5 per cent. at 18° C.

[2] For CO, E. Wiedemann, from Landolt and Börnstein, p. 339:
From 23°–99° C., 0.2425 *cal/gram*, at constant pressure;
" 26°–198° C., 0.2426 " " " "
For O_2, Regnault: *loc. cit.*:
From 13°–207° C., 0.2175 *cal/gram*, at constant pressure.
For CO_2, E. Wiedemann and H. Le Chatelier: Zeitschr. phys. Chem. **2**, 783 (1888).

whereby it is overlooked that the two oxides participate in the reaction in *bimolecular* quantities. This oversight invalidates Le Chatelier's results.

Having now in (16) the heat of dissociation as a function of the temperature, the complete expression (13) for $\Delta \log K$ can be written

$$\log_{10} K_2 - \log_{10} K_1 = \frac{1}{4.6}\int_{T_1}^{T_2}\left(\frac{133963}{T^2} + \frac{7.393407}{T} - 0.011077\right).\partial T$$

$$= 29122.3\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + 3.696703 \log_{10}\frac{T_2}{T_1} + 0.002408(T_1 - T_2). \quad (17)$$

This expression gives the characteristic equilibrium-constant for any assigned temperature, when some one K_1 for a corresponding T_1 is known. For this latter we may suitably select the determination of Deville, cited by Le Chatelier,[1] that the percentage dissociation a is forty per cent. at 3000° C. under atmospheric pressure.

The formula for K, *i. e.* the reaction-isotherm, for the dissociation reaction

$$2CO_2 \rightleftarrows 2CO + O_2,$$

is

$$K.C^2 = c_1^2.c_2$$

for the respective molecular concentrations; this may be written

$$K.\left(\frac{1-a}{v}\right)^2 = \left(\frac{a}{v}\right)^2.\frac{a}{v}$$

or

$$K = \frac{a^3}{(1-a)^2 v},$$

in which v is the volume of the system, but since for the total pressure $Pv = (2+a)RT$, and $R = 0.0819$ liter × atmospheres, we obtain

$$K = \frac{a^2 P}{(1-a)^2(2+a)\,0.0819\,T}. \quad (18)$$

Inserting the values above given, $a = 0.40$, $T = 3273$, $P = 1.00$, we have as starting-point for the calculation of equilibria,

$$\log_{10} K_1 = \bar{4}.441436;$$

with this value in (17) we get our fundamental function in the desired form representing $\log K_2$ as a function of the temperature alone. The result of the calculation for a series of temperatures is as follows:

[1] Ztschr. phys. Chem. **2**, 782 (1888).

Temperature.	$\log_{10} K$.	*Temperature.*	$\log_{10} K$.
1000° C.	$\bar{15}.762175$	3000°C.	$\bar{4}.441436$
1300	$\bar{11}.742573$	3300	$\bar{4}.606911$
1500	$\bar{9}.541564$	3500	$\bar{4}.644804$
2000	$\bar{6}.349543$	3555	$\bar{4}.646496$ (max.)
2500	$\bar{5}.774939$	4000	$\bar{4}.543778$

This change of the equilibrium-ratio K with the temperature is more readily seen from the accompanying curve, Fig. 1.

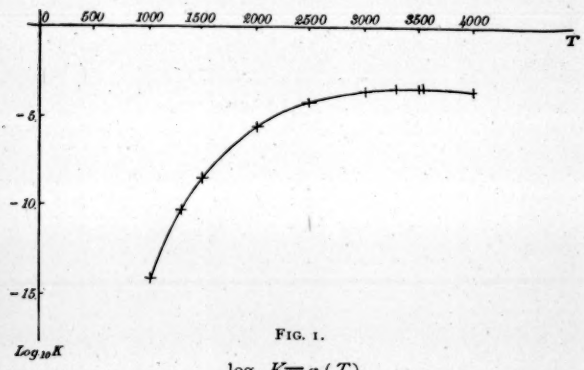


FIG. 1.

$$\log_{10} K = \varphi(T).$$

A pronounced maximum of the function near 3500° C. is shown by both the table and the plat, its appearance is due to the fact that at this temperature the value of Q, the heat of dissociation, passes through zero and changes its sign. This is clearly shown by the calculation of Q in its dependence upon T, from equation (16), whereby the following series of values is obtained:

Successive Values of the Heat of Dissociation.

T.	$\frac{1}{4}Q$.	T.	$\frac{1}{4}Q$.
0° C.	+ 67578 *cal.*	2000° C.	+ 46767 *cal.*
18	67588	2500	34640
500	66508	3000	19742
1000	62662	3555	± 0
1500	56125	4000	— 18343

The relation of the heat of reaction to the temperature is seen more readily from the curve of $Q=\varphi(T)$ here appended, see Fig. 2.

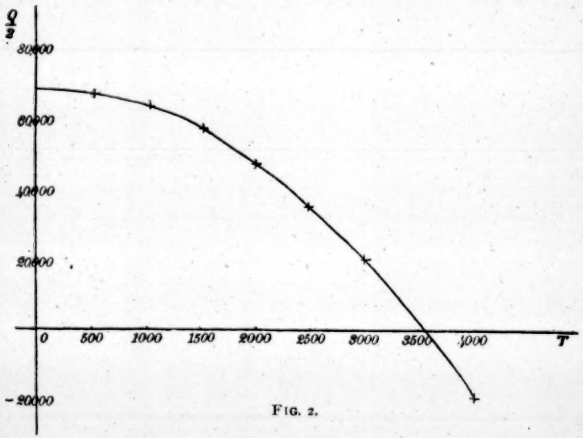


FIG. 2.

$$\tfrac{1}{2}Q=\varphi(T).$$

Since Q vanishes at 3555° C., the value of the differential coefficient $\frac{\partial \log_e K}{\partial T}$ also vanishes, and consequently both log K and the degree of dissociation at any given pressure become maxima simultaneously.

From the above K-values the percentage dissociation α for any given total pressure at any assigned temperature is directly calculable by employment of (18), which must for the purpose be solved for α. We thus obtain, setting for convenience the symbol $\mathfrak{S}$ for the quantity

$$\mathfrak{S}=\frac{-RTK}{RTK-\boldsymbol{P}},$$

$$\alpha=[\mathfrak{S}+\sqrt{\mathfrak{S}^2+\mathfrak{S}^2}]^{\frac{1}{2}}+[\mathfrak{S}-\sqrt{\mathfrak{S}^2+\mathfrak{S}^2}]^{\frac{1}{2}}. \qquad (19)$$

The final values, obtained by the use of this formula, for most of the above temperatures and a series of total pressures are collected in the following table:

Dissociations, in Entire Percentages.

Temp.	0.001 atm.	0.01	0.1	1.0	10.0	100.
1000° C.	0.11	0.05	0.024	0.011	0.005	0.0024
1500	9.5	4.6	2.2	1.0	0.5	0.2
2000	57.7	34.7	18.3	9.0	4.3	2.0
2500	87.0	69.6	46.0	25.7	13.0	6.3
3000	93.9	83.4	62.7	(40.0)	21.6	10.8
3500	95.4	87.0	69.7	46.1	25.7	13.0
3555	95.4	87.1	69.8	46.2	25.8	13.1
4000	95.1	86.4	68.6	45.0	24.9	12.6

The maximum values at 3555° C., as shown by the table, are very marked. The possibility of their existence was recognized by Le Chatelier, although his error in calculating $Q = \varphi(T)$ prevented a determination of this temperature and of the dissociations corresponding to it. Yet he clearly pointed out, as indicated above, that since Q decreases continuously with rising temperature, the quantity $\frac{Q}{T^2}$ must decrease still more rapidly, and the integral $\int \frac{Q}{T^2} . \partial T$ must in consequence increase decreasingly as the temperature goes up, becoming a maximum when $Q = 0$.

The only very reliable experimental values of 100α known to the writers are the following:

1300° C.	1 atm.	theory 0.24	obs'd $>$0.2, Deville.
1500	1	1.00	$<$1.0, Crafts.
2000	6	5.00	$<$5.0, Mallard & Le Chatelier.

The agreement between theory and experiment seems to be fully as good as that reached by Le Chatelier for the same temperatures. It will be noted in general that very high dissociations correspond to high temperatures and low pressures, and extremely low ones are found when these conditions are reversed. A good idea of the general relations may be had from the plat of the dissociation-values at different temperatures and pressures; see Fig. 3.

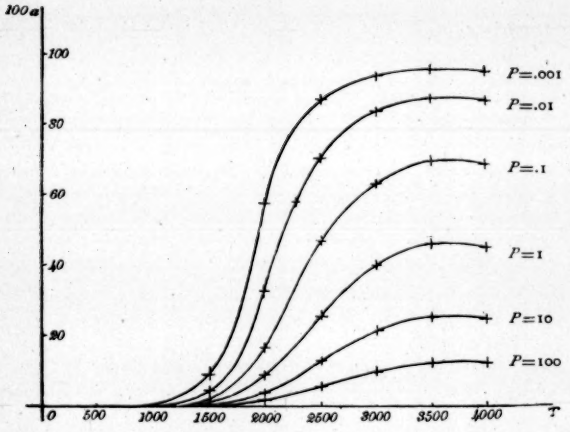


FIG. 3.

$$100\,a = \varphi\,(T, P).$$

The absolute maximum of decomposition, which may be reached in dissociation-reactions which are not accompanied by a change of volume, and which are therefore functions of the temperature alone,[1] does not find its counterpart in dissociations of this type. With falling pressure, especially at the higher temperatures, the degree of dissociation seems to approach one hundred per cent. as a limit.

CORNELL UNIVERSITY, *September*, 1894.

[1] **Planck**: Ann. der Phys. Wied. **31**, 198 (1887). The fact of a maximum dissociation follows simply enough from the fact that the equilibrium is independent of the volume. Being thus only a function of the temperature, $\frac{a}{(1-a)} = K = \phi\,(T)$, the dissociation cannot become complete unless K becomes infinite, that is, unless Q becomes infinite—which is impossible.

A NEW FORMULA FOR SPECIFIC AND MOLECULAR REFRACTION.

By W. F. Edwards.

Since Biot and Arago in the year 1806 undertook the verification of the Newton-Laplace formula, $\frac{m^2-1}{d} = K$ (a constant), much has been done and much has been written on the relation of the index of refraction to the density of a substance. Although the theoretical arguments for this formula failed to apply after the establishment of the undulatory theory, still the formula was the subject of experiment from time to time and retained a value as an empirical physical law, probably because Biot and Arago had found it to hold so closely for the gases which they examined.

Gladstone and Dale,[1] while trying to verify the Newton-Laplace law when applied to liquids, found that the formula $\frac{m-1}{d} = K$ was much more nearly in accord with their experiments. Landolt, studying the relations of the numbers obtained by using the Gladstone formula multiplied by the molecular weight of the substance, found that the molecular refraction—as the numbers thus found were designated—is the sum of the atomic refractions of the elements of which it is composed. Later, Brühl found that when carbon is united ethylene-wise the molecular refraction is greater than the sum of the atomic refractions of the elements composing the substance. Moreover, Landolt[2] applied this empirical formula to mixtures and found that the equation $\frac{P(M-1)}{D} = \frac{p(m-1)}{d} + \frac{p_1(m_1-1)}{d_1} + \frac{p_2(m_2-1)}{d_2} +$ etc. held very closely for the mixtures tried; M, P, and D being, respectively, the index of refraction, weight, and density of the mixture, and m, m_1, m_2, etc., p, p_1, p_2, etc., d, d_1, d_2, etc., being the corresponding properties of the components. Using this equation with two terms in the second member he was able to determine the percentage of each of the components by optical analysis.

It may be stated then that the importance of the relations between the index of refraction and the density on the one hand, and the index of refraction and molecular and atomic weights on the other hand, have been established by using an empirical formula.

[1] Phil. Trans. Lond. 1858.

[2] Ann. Chem. (Liebig) Suppl. 4, 1.

After the establishment of the undulatory theory there was no formula showing the relation between the index of refraction and the density of a substance that had a theoretical foundation until the year 1880. In this year there appeared two translations in *Wiedemann's Annalen*,[1] the first, of a paper by H. A. Lorentz, of Amsterdam, in which he shows that $\frac{(m^2-1)}{(m^2+2)d}=K$, having derived this formula from a mathematical consideration of the electromagnetic theory of light; the second being the translation of a paper by L. Lorenz, of Copenhagen, in which he shows that $\frac{(m^2-1)}{(m^2+2)d}=K$, having derived this formula from a mathematical consideration of the undulatory theory of light. Since these papers appeared there has been much work done in comparing the merits of the two formulæ, $\frac{(m-1)}{d}$ and $\frac{(m^2-1)}{(m^2+2)d}$, both being assumed constants for any particular substance. The result of these comparisons has been that neither formula seems to be entirely in accord with observation, the one proving to be more concordant in some instances and the other in others.

In the year 1885 Dufet[2] furnished a theoretical demonstration of Gladstone's law, and another was furnished in the year 1889 by Sutherland.[3] Meanwhile another formula, $(m^2-1).(v-b)=C(1+\frac{a}{e^{kT}})$ appeared,[4] but has not been the subject of much experimental verification.

Since there has been no formula entirely in accord with all known facts after so much mathematical and theoretical demonstration, I think I shall not be presuming too much if I offer another formula which has at least the merit of simplicity of demonstration. It asks no question as to the size and shape of molecules, but simply assumes that light is transmitted faster *in vacuo* than elsewhere, and that the diminution of the rate depends on the amount and kind of material in unit volume and upon its physical state.

Taking the well-known equation for the index of refraction

$$M=\frac{\sin i}{\sin r}=\frac{V}{V_1}, \qquad (1)$$

where V is the velocity of light in the ether of space, and V_1 is the velocity in the substance, then if we call the difference between V and V_1 A, we have $MV-MA=V$ or $\frac{(M-1)V}{M}=A$.

[1] 9, 642 and 11, 77. [2] J. de phys. 1885, 447. [3] Phil. Mag. 27, 141.
[4] Ketteler: Ann. der Phys. Wied. 33 and 35 (1888).

If the difference, A, is proportional to the amount of substance, and if we assume as the unit one gram of substance in one cubic centimeter, and that X is the retardation of velocity for a unit of substance,

$$X = \frac{(M-1)\ V}{MD}, \qquad (2)$$

where M is the index of refraction and D is the specific gravity of the substance.

If there are several substances in a mixture for which $\frac{(M-1)V}{MD} = C$, C being the retardation of V by the mixture, and $\frac{(m-1)V}{md} = a$, $\frac{(m_1-1)V}{m_1d_1} = b$, $\frac{(m_2-1)V}{m_2d_2} = c$, etc., are the corresponding equations for the components, then $C = pa + p_1b + p_2c +$ etc., where $p + p_1 + p_2 +$ etc. $= 1$ and represent the percentage of the several components of the mixture. Since V is a factor of both members of the equation, it may be written in the form

$$\frac{(M-1)}{MD} = \frac{p\,(m-1)}{md} + \frac{p_1(m_1-1)}{m_1d_1} + \frac{p_2(m_2-1)}{m_2d_2} + \text{etc.} \qquad (3)$$

I.—Table showing the specific refraction of some substances when the density is changed by changing the temperature, for the formula $\frac{(M-1)}{MD}$.

Temperature.	Substance.	Physical state.	Specific gravity at $\frac{t°}{4°}$.	Index of refraction for sodium light.	$\frac{(M-1)}{MD}$	From the data of
0°	Water.	Liquid.	0.99987	1.33411	0.2504	Ketteler.
20	"	"	0.99824	1.33327	0.2503	"
40	"	"	0.99233	1.33093	0.2504	"
60	"	"	0.98331	1.32753	0.2509	"
80	"	"	0.97191	1.32330	0.2513	"
100	"	"	0.95863	1.31843	0.2519	"
100	"	Vapor.	0.000806	1.00025	0.3101	Lorenz.
0	Ethyl alcohol.	Liquid.	0.8056	1.36962	0.3339	Ketteler.
10	" "	"	0.7972	1.36565	0.3347	"
20	" "	"	0.7887	1.36164	0.3355	"
100	" "	Vapor.	0.00206	1.000873	0.4234	Lorenz.
10	Chloroform.	Liquid.	1.516	1.4490	0.2044	Gladstone.
20	"	"	1.4898	1.4467	0.2072	Haagen.
30	"	"	1.479	1.4397	0.2064	Gladstone.
100	"	Vapor.	0.00535	1.00144	0.2691	Lorenz.
10	Carbon disulphide.	Liquid.	1.2793	1.6344	0.3034	Gladstone.
24.5	" "	"	1.2593	1.6235	0.3049	"
30	" "	"	1.2494	1.6213	0.3067	"
100	" "	Vapor.	0.0034	1.00148	0.4347	Lorenz.
2	Benzene.	Liquid.	0.8979	1.5122	0.3772	Gladstone.
10	"	"	0.8868	1.5029	0.3772	"
21.5	"	"	0.8773	1.4979	0.3775	"

It will be observed that there is quite generally an increase in $\frac{(M-1)}{MD}$ as the temperature rises, and that there is a marked increase for the vapor in every case. This increase with rise of temperature and change of physical state will be the subject matter of a future paper which is already outlined.

II.—Table comparing the two members of the equation $\frac{(M-1)}{MD} = \frac{p(m-1)}{md} + \frac{p_1(m_1-1)}{m_1 d_1}$, for some ordinary aqueous solutions.

Temperature.	Per cent. of substance dissolved.	Specific gravity (D).	Index of refraction for sodium light (M).	$\frac{(M-1)}{MD}$.	$\frac{p(m-1)}{md} + \frac{p_1(m_1-1)}{m_1 d_1}$.	Difference for fourth decimal place.	From the data of
	Glycerin $\frac{15°}{15°}$						
15°	00	1.000	1.3330	0.2498	0.2498	00	Skalweit.
"	10	1.0240	1.3452	0.2506	0.2502	04	"
"	20	1.0490	1.3581	0.2513	0.2506	07	"
"	30	1.0750	1.3715	0.2520	0.2510	10	"
"	40	1.1020	1.3854	0.2524	0.2513	11	"
"	50	1.1290	1.3996	0.2529	0.2518	11	"
"	60	1.1570	1.4144	0.2533	0.2521	12	"
"	70	1.1855	1.4295	0.2534	0.2525	09	"
"	80	1.2125	1.4444	0.2537	0.2529	08	"
"	90	1.2396	1.4595	0.2540	0.2533	07	"
"	100	1.2650	1.4742	0.2537	0.2537	00	"
	Acetic acid $\frac{20°}{4°}$						
20	00.00	0.9982	1.33327	0.2492	0.2492	00	Ketteler.
21.5	4.65	1.0065	1.33554	0.2496	0.2493	03	Edwards.
"	9.26	1.0130	1.33934	0.2501	0.2501	00	"
"	13.97	1.0203	1.34221	0.2499	0.2502	03	"
20	20.72	1.0296	1.34637	0.2499	0.2508	09	Damien.
21.5	29.45	1.0418	1.35222	0.2500	0.2517	17	Edwards.
20	41.49	1.0532	1.35878	0.2524	0.2524	00	Damien.
"	51.81	1.0601	1.36374	0.2516	0.2532	16	"
"	62.50	1.0640	1.36835	0.2529	0.2541	12	"
"	68.97	1.0672	1.37120	0.2537	0.2546	09	"
"	76.92	1.0690	1.37443	0.2549	0.2552	03	"
"	89.96	1.0673	1.37624	0.2561	0.2561	00	"
21.5	94.33	1.0664	1.37442	0.2554	0.2566	12	Edwards.
"	99.44	1.0554	1.37029	0.2561	0.2570	09	"
20	100.00	1.0507	1.37022	0.2571	0.2571	00	Damien.
	Ammonia $\frac{15°}{15°}$						
16	00.00	1.0000	1.33311	0.2498	0.2498	00	Edwards.
"	4.20	0.9816	1.33546	0.2559	0.2553	06	"
"	10.27	0.9587	1.33817	0.2636	0.2632	04	"
"	14.63	0.9434	1.34071	0.2693	0.2711	18	"
"	19.99	0.9256	1.34397	0.2766	0.2757	09	"
"	23.98	0.9130	1.34597	0.2615	0.2807	08	"
00	100.00	0.00077	1.000384	0.4982	0.4982	00	Dulong.

Temperature.	Per cent. of substance dissolved.	Specific gravity (D).	Index of refraction for sodium light (M).	$\frac{(M-1)}{MD}$.	$\frac{p_1(m-1)}{md} + \frac{p_2(m_1-1)}{m_1 d_1}$	Difference for 4th decimal place.	From the data of
	Hydrochloric acid, $\frac{16°}{4°}$						
16	00.00	0.9981	1.33311	0.2498	0.2498	00	Edwards.
"	5.31	1.0261	1.34522	0.2502	0.2497	05	"
"	10.62	1.0527	1.35725	0.2501	0.2496	05	"
"	16.55	1.0814	1.35067	0.2501	0.2495	06	"
"	23.28	1.1160	1.38723	0.2508	0.2490	18	"
"	30.45	1.1530	1.40350	0.2500	0.2488	12	"
"	37.17	1.1887	1.41858	0.2484	0.2490	06	"
0	100.00	1.00162	1.000447	0.2764	0.2764	00	Mascart.
	Alcohol $\frac{20°}{15°.5}$						
18	00.00	0.9981	1.33300	0.2495	0.2495	00	Edwards.
"	3.82	0.9922	1.33512	0.2529	0.2537	08	"
"	12.00	0.9801	1.34088	0.2593	0.2596	02	"
"	20.00	0.9695	1.34683	0.2656	0.2661	05	"
"	25.60	0.9627	1.35000	0.2693	0.2708	15	Landolt.
"	28.63	0.95697	1.35231	0.2722	0.2733	11	Edwards.
"	37.44	0.9408	1.35697	0.2796	0.2807	11	"
"	46.90	0.9212	1.35970	0.2872	0.2885	13	"
"	50.70	0.9168	1.3609	0.2893	0.2917	24	Landolt.
"	56.77	0.8991	1.36233	0.2966	0.2970	04	Edwards.
"	67.67	0.8737	1.36381	0.3053	0.3059	06	"
"	74.90	0.8603	1.36350	0.3099	0.3148	49	Landolt.
"	79.12	0.8464	1.36451	0.3166	0.3154	02	Edwards.
"	92.15	0.8128	1.36283	0.3275	0.3253	22	"
"	98.41	0.7948	1.36095	0.3337	0.3365	28	"
22	100.00	0.7964	1.36060	0.3328	0.3328	00	Landolt.

In Table II the data of Damien have indices of refraction for ***hydrogen*** *a* instead of sodium light.

III.—Table comparing the specific refraction $\frac{(M-1)}{MD}$ and the molecular refraction $\frac{P(M-1)}{MD}$ of some organic compounds.

Temperature.	Substance.	Specific gravity.	Index of refraction for sodium light.	$\frac{(M-1)}{MD}$	$\frac{P(M-1)}{MD}$.	Difference for CH_2.	From data of
	Hydrocarbons $\frac{16°}{0°}$.						
	methane.	0.000718	1.000443	0.6106	9.77		Dulong.
16°	pentane.	0.6174	1.35830	0.4270	30.74	5.24	Bartoli and Stracciati.
"	hexane.	0.6765	1.38547	0.4112	35.36	4.62	"
"	heptane.	0.7144	1.40362	0.4025	40.25	4.89	"
"	octane.	0.7290	1.41202	0.4002	45.62	5.37	"
"	nonane.	0.7457	1.42073	0.3971	50.82	5.20	"
"	decane.	0.7561	1.42574	0.3949	56.07	5.25	"

Temperature.	Substance.	Specific gravity.	Index of refraction for sodium light.	$\frac{(M-1)}{MD}$.	$P\left(\frac{M-1}{MD}\right)$.	Difference for CH_2.	From data of
	Hydrocarbons $\frac{16°}{0°}$.						
16°	undecane.	0.7673	1.43136	0.3928	61.27	5.20	Bartoli and Stracciati.
"	dodecane.	0.7769	1.43676	0.3913	66.52	5.25	"
"	tridecane.	0.7881	1.44227	0.3891	71.58	5.06	"
"	tetradecane.	0.7824	1.44809	0.3919	77.59	6.01	"
"	pentadecane.	0.8096	1.45319	0.3852	81.86	4.27	"
"	hexadecane.	0.8167	1.45697	0.3840	86.78	4.92	"
	Alcohols $\frac{20°}{4°}$.		for Ha.				
20	methyl.	0.7953	1.3279	0.3105	9.93		Landolt.
"	ethyl.	0.8000	1.36050	0.3312	15.23	5.30	".
"	propyl nor.	0.8044	1.3835	0.3446	20.67	5.44	Brühl.
"	butyl nor.	0.8099	1.3971	0.3509	25.96	5.29	"
"	amyl ferm.	0.8123	1.4057	0.3553	31.26	5.30	Landolt.
	Aldehydes $\frac{20°}{4°}$.						
20	acetic.	0.7799	1.32980	0.3180	13.99		Landolt.
"	propylic.	0.8066	1.3616	0.3292	19.10	5.11	Brühl.
"	butyl.	0.8170	1.3822	0.3384	24.36	5.26	"
"	valeric.	0.7984	1.3861	0.3488	29.99	5.63	Landolt.
"	heptoic.	0.8495	1.4234	0.3501	39.91	4.96	Brühl.
	Acids $\frac{20°}{4°}$.						
20	formic.	1.2188	1.3693	0.2213	10.28		Landolt.
"	acetic.	1.0495	1.3699	0.2573	15.44	5.16	"
"	propionic.	0.9946	1.3846	0.2793	20.66	5.22	"
"	butyric.	0.9594	1.3955	0.2954	25.99	5.33	"
"	valeric (iso.)	0.9298	1.4022	0.3085	31.45	5.46	"
"	heptoic.	0.9160	1.4192	0.3224	41.91	5.23	"
	Esters $\frac{20°}{4°}$.						
20	methyl valerate.	0.8795	1.3927	0.3207	37.20		Landolt.
"	ethyl valerate.	0.8661	1.3950	0.3270	42.51	5.31	"
"	amyl valerate.	0.8568	1.4098	0.3392	58.34	5.27	"
"	methyl acetate.	0.9039	1.3592	0.2923	21.63	5.25	"
"	methyl butyrate.	0.8962	1.3869	0.3113	31.75	5.06	"
"	methyl valerate.	0.8795	1.3927	0.3207	37.20	5.45	"
"	ethyl formate.	0.9064	1.3580	0.2908	21.52	5.23	"
"	ethyl acetate.	0.9007	1.3707	0.3003	26.42	4.93	"
"	ethyl butyrate.	0.8892	1.3940	0.3177	36.85	5.23	"
"	ethyl valerate.	0.8661	1.3950	0.3270	42.51	5.66	"

Temperature.	Substance.	Specific gravity.	Index of refraction for sodium light.	$\frac{(M-1)}{MD}$.	$\frac{P(M-1)}{MD}$.	Difference for CH_2.	From data of
	Esters $\frac{20°}{4°}$.						
14°	ethyl iodide.	1.9313	1.5067	0.1741	27.16		Gladstone.
16	propyl iodide.	1.7508	1.4979	0.1899	32.28	5.12	"
"	isobutyl iodide.	1.5982	1.4874	0.2039	37.52	5.24	"
14	amyl iodide.	1.5048	1.4884	0.2180	43.56	5.64	"
	Amines $\frac{20°}{4°}$.						
14	diethyl.	0.7092	1.3824	0.3887	17.49		Gladstone.
"	triethyl.	0.7317	1.3957	0.3861	28.18	5.34	"
23.5	propyl.	0.7140	1.3827	0.3907	23.05	5.13	"
23.2	dipropyl.	0.7356	1.3983	0.3907	39.46	5.47	"
22.8	tripropyl.	0.7535	1.4121	0.3905	55.84	5.28	"
	Aromatic Compounds:						
10	benzene.	0.8903	1.5078	0.3711	28.94		"
"	toluene.	0.8704	1.4982	0.3754	34.53	5.53	"
18	xylene.	0.8632	1.4966	0 3773	40.00	5.47	"
19	mesitylene.	0.8632	1.4960	0.3759	45.11	5.10	"
12	cumene.	0.8432	1.4801	0.3785	45.42	5.42	"
21	phenol.	1.0598	1.5509	0.3282	30.85		"
"	cresol.	1.0390	1.5419	0.3318	35.83	4.98	"
"	metacresol.	1.033	1.5364	0.3313	35.78	4.93	"

The numbers representing the molecular refraction $\frac{P(M-1)}{MD}$ of the paraffins show for each addition of CH_2 an average increase for the

Hydrocarbons.	Alcohols.	Aldehydes.	Acids.	Iodides.	Ethereal Salts.	Amines.	All taken together.
5.11	5.33	5.24	5.28	5.33	5.31	5.24	5.28

This general average difference is very nearly that found from heptane to tridecane among the hydrocarbons, although the average difference for the hydrocarbons is lower than in any other group. The average difference for the aromatic compounds is 5.24. In the case of the ethereal salts it will be noticed that if we compare the numbers for the molecular refraction with corresponding ones for the acids themselves, the difference for CH_2 is greater than the average found from the table. For example, methyl acetate, methyl butyrate, and methyl valerate give, respectively, the numbers 21.63, 31.75 and 37.20; while the corresponding acids give the numbers 15.44, 25.99 and 31.45; the

difference between the salt and acid being 6.19, 5.76 and 5.65, respectively—an average of 5.86 for all.

As another example we may take ethyl formate, ethyl acetate, ethyl butyrate and ethyl valerate, which give the numbers 21.52, 26.42, 36.85 and 42.51; while the numbers for the corresponding acids are 10.28, 15.44, 25.99 and 31.45; showing differences respectively of 5.62, 5.49, 5.43 and 5.53—an average of 5.52. It will be understood that the average 5.52 corresponds with the average 5.86, being $\frac{(5.26 + 5.86)}{2}$.

The numbers found for molecular refraction by using the Lorenz-Lorentz formula $\frac{P(M-1)}{(M+2)D}$ shows a greater difference for a difference of CH_2 when acids and ethereal salts are compared than is otherwise found, as the following numbers taken from Landolt's paper[1] show:

Formic acid,	8.52;	ethyl formate,	17.93;	difference for CH_2,	4.71.
Acetic "	12.93;	methyl acetate,	18.03;	" " "	5.10.
" "	12.93;	ethyl "	22.14;	" " "	4.61.
Butyric "	22.01;	methyl butyrate,	26.79;	" " "	4.78.
" "	22.01;	ethyl "	31.20;	" " "	4.58.
Valeric "	26.72;	methyl valerate,	31.46;	" " "	4.74.
" "	26.72;	ethyl "	35.98;	" " "	4.63.

An average difference of 4.75, instead of 4.56 which Landolt finds for CH_2 by comparing groups of alcohols, aldehydes, acids and ethereal salts in the usual way.

Landolt, using the Lorenz-Lorentz formula, found for the four groups mentioned an average difference of—

4.61 for an increase of CH_2 among the alcohols,
4.57 " " " " the aldehydes,
4.56 " " " " the acids,
4.48 " " " " the ethereal salts.

The general average for the four groups is 4.56. There is a difference of 0.13 between the highest and lowest average difference, which is 2.85 per cent. of 4.56, the general average difference. For corresponding groups in Table III, the average difference for CH_2 is 5.29, with a difference of 0.09 between the highest and lowest average difference, which is 1.7 per cent. of 5.29, the general average difference. The numbers in Table III have been taken from the same data and therefore show less percentage error than the Lorenz-Lorentz formula, which Brühl has shown to give less percentage error than the Gladstone formula.

[1] Ann. Chem. (Leibig) **213**, 101.

IV.—Table comparing the specific refraction $\frac{(M-1)}{MD}$ and molecular refraction $\frac{P(M-1)}{MD}$, of some isomeric organic compounds.

Substance.	Specific gravity.	Index of refraction for Hα.	$\frac{(M-1)}{MD}$.	$\frac{P(M-1)}{MD}$.	Difference.	From the data of
Allyl alcohol.	0.8563	1.4111	0.3402	19.73	0.46	Gladstone.
Acetone.	0.7920	1.3572	0.3323	19.27	0.46	Landolt.
Propyl aldehyde.	0.8066	1.3613	0.3292	19.10	0.17	Brühl.
Methyl acetate.	0.9039	1.3592	0.2923	21.63		Landolt.
Ethyl formate.	0.9064	1.3580	0.2908	21.52	0.11	"
Normal propyl alcohol.	0.8044	1.3835	0.3446	20.67		Brühl.
Isopropyl alcohol.	0.7887	1.3757	0.3465	20.79	0.12	"
Butyric aldehyde.	0.8170	1.3822	0.3384	24.36		"
Isobutyric aldehyde.	0.7938	1.3709	0.3408	24.53	0.17	"
Normal butyric acid.	0.9587	1.3958	0.2957	26.02		"
Isobutyric acid.	0.9490	1.3909	0.2961	26.05	0.03	"
Ethyl acetate.	0.9007	1.3707	0.3003	26.42	0.37	Landolt.
Normal butyl alcohol.	0.8099	1.3971	0.3509	25.96		Brühl.
Isobutyl alcohol.	0.8062	1.3940	0.3506	25.94	0.02	Landolt.
Trimethyl carbinol.	0.7864	1.3857	0.3539	26.18	0.24	Brühl.
Ethyl acetate.	0.7157	1.3511	0.3620	26.78	0.60	Landolt.
Valeric acid.	0.9298	1.4022	0.3085	31.45		"
Methyl butyrate.	0.8962	1.3869	0.3113	31.75	0.30	"
Propyl acetate.	0.8856	1.3824	0.3123	31.85	0.10	Brühl.
Caproic acid.	0.9237	1.4116	0.3156	36.61		Landolt.
Methyl valerate.	0.8795	1.3927	0.3207	37.20	0.59	"
Ethyl butyrate.	0.8892	1.3940	0.3177	36.85	0.35	"
Amyl formate.	0.8802	1.3959	0.3222	37.37	0.52	"
Methyl citraconate.	1.1164	1.4504	0.2782	43.96		Gladstone.
Methyl mesaconate.	1.1246	1.4564	0.2786	44.02	0.06	"
Ethyl citraconate.	1.0480	1.4459	0.2942	54.72		"
Ethyl mesaconate.	1.0500	1.4499	0.2955	54.96	0.24	"
Ethylene chloride.	1.2521	1.4419	0.2447	24.22		Brühl.
Ethylidene chloride.	1.1743	1.4142	0.2494	24.69	0.47	"
Ethylene chloride.	1.2720	1.4485	0.2422	23.97		Gladstone.
Ethylidene chloride.	1.2010	1.4237	0.2477	24.53	0.56	"
Propyl bromide.	1.3520	1.4313	0.2229	27.31		Brühl.
Isopropyl bromide.	1.3097	1.4223	0.2267	27.88	0.57	"
Propyl iodide.	1.7508	1.5069	0.1921	32.65		Gladstone.
Isopropyl iodide.	1.7157	1.5040	0.1953	33.20	0.55	"
Propyl iodide.	1.7427	1.5008	0.1914	32.54	0.66	Brühl.
Isopropyl iodide.	1.7033	1.4952	0.1951	33.17	0.63	"
Paraxylene.	0.8488	1.4846	0.3846	40.77		Gladstone.
Orthoxylene.	0.8632	1.4966	0.3844	40.75	0.02	"
Metaxylene.	0.8726	1.5020	0.3830	40.60	0.15	"
Cresol.	1.0390	1.5419	0.3382	36.52		"
Metacresol.	1.0330	1.5364	0.3380	36.50	0.02	"
Benzyl alcohol.	1.0412	1.5370	0.3356	36.25	0.25	"
Benzyl chloride.	1.0990	1.5415	0.3196	40.43		"
Chlorotoluene.	1.0761	1.5271	0.3207	40.57	0.14	"
Aniline.	1.0160	1.5828	0.3617	33.64		"
Picoline.	0.9409	1.5006	0.3545	32.97	0.67	"

In this table, where the data are from Gladstone, the indices of refraction are for sodium light.

In a future paper I intend giving much more in detail the application of this formula to chemical problems. This paper is considered as a preliminary notice of the formula and contains only tables enough to show that there is sufficient experimental verification to warrant further work with this formula.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.

Contribution from the Chemical Laboratory of the University of Kansas.

ON PARAISOBUTYLSALICYL ALDEHYDE AND SOME OF ITS DERIVATIVES.

BY F. B. DAINS AND I. R. ROTHROCK.

This is the continuation of some work carried on by W. P. Bradley and one of us (D) in the laboratory of Wesleyan University, "On the action of acetyl chloride on orthohydroxy aldehydes."[1] It was deemed desirable to see whether an orthohydroxy aldehyde containing a substituted isobutyl group would condense to a substituted disalicyl aldehyde as readily as if it had contained a methyl or an ethoxy group. This necessitated preparing paraisobutylsalicyl aldehyde.

The starting-point for the research was paraisobutyl phenol. This was prepared according to Liebmann[2] by heating a mixture of phenol, isobutyl alcohol and zinc chloride to 180°. The product, freed from zinc chloride by pouring into water acidified with hydrochloric acid, is distilled, and the fraction between 220°–245° on a second distillation gives practically pure isobutyl phenol. It was found best to continue the heating with zinc chloride until the liquid showed a tendency to separate into two layers; otherwise the yield would be decreased.

The fraction above 245° was found on examination to contain a quantity of an alkali-insoluble body. This was isolated by

[1] This Journal **14**, 293; Ber. d. chem. Ges. **22**, 1134.
[2] Ber. d. chem. Ges. **14**, 1845; **15**, 150.

shaking out the alkaline solution with benzene. On drying and distilling the bulk of the oil passed over between 263° and 268° at 734 mm. pressure.

Analysis.

I. 0.2940 gram oil gave 0.2774 gram H_2O and 0.8780 gram CO_2.

II. 0.2766 gram oil gave 0.2605 gram H_2O and 0.7900 gram CO_2.

	Calculated for $C_{14}H_{22}O$.	Found. I.	II.
C	81.55	81.44	81.50
H	10.58	10.48	10.47

These results indicated that the oil was doubtless the isobutyl ether of isobutyl phenol, $C_4H_9.C_6H_4.OC_4H_9$. To prove the identity some of the ether was prepared synthetically. The sodium salt of isobutyl phenol (1 mol.) dissolved in water was boiled for several hours with isobutyl iodide (1 mol.). The oil formed was separated out, dried over calcium chloride and distilled. Between 264°–266° at 736 mm. pressure there came over an oil which in all its properties resembled the ether previously obtained.

Analysis.

0.2330 gram substance gave 0.6958 gram CO_2 and 0.2230 gram H_2O.

	Calculated for $C_{14}H_{22}O$.	Found.
C	81.55	81.46
H	10.58	10.63

The isobutyl ether of isobutyl phenol is a clear, slightly yellow oil, lighter than water—in which it is insoluble—and slowly volatile with steam. It does not solidify at —18° and refracts light strongly.

Its formation along with isobutyl phenol is due to a secondary reaction between the isobutyl alcohol and isobutyl phenol, water splitting off the hydroxyl groups and forming the ether. The longer the heating is continued in the first place the greater the amount of ether produced.

To prepare the aldehyde the following mixture was heated on the water-bath for about two hours:

45 grams isobutyl phenol, 45 grams caustic soda or 75 grams potash, 55 grams chloroform, 500 cc. water.

The chloroform was added slowly, the color meanwhile changing to a deep red, with the formation of tar. The contents of several flasks were united, acidified with sulphuric acid and distilled with steam. A mixture of unchanged isobutyl phenol and paraisobutyl salicylic aldehyde came over slowly. The distillate was shaken out with ether, the ether dried over calcium chloride and distilled off, leaving an oil behind.

Efforts to separate this mixture of phenol and aldehyde by ordinary means were fruitless. Acid sodium sulphite gives no satisfactory results, and the boiling-points of the two compounds are too near together to admit of separation by fractional distillation. Experiment showed, however, that phenylhydrazine reacted with great ease upon this mixture. When added to the oil directly, heat is evolved and the oil solidifies. The best results are obtained when the mixture of phenol and aldehyde is dissolved in alcohol and one-fourth its weight of phenylhydrazine in alcoholic solution is added. There separates out almost immediately the yellow precipitate of the hydrazone. This is filtered off with the aid of a suction-pump and purified by crystallization from alcohol or petroleum-ether. The pure paraisobutylsalicyl hydrazone is a stable body, but when treated with half-strength sulphuric acid and distilled with steam, breaks up into phenylhydrazine sulphate and paraisobutylsalicyl aldehyde. This steam-distillate was extracted with ether, dried and distilled. After the ether was off, the mercury rose rapidly, and between 251°–252° at 729 mm. pressure the bulk of the residual oil passed over.

Analysis.

I. 0.3785 gram oil gave 0.2681 gram H_2O and 1.0275 grams CO_2.

II. 0.2507 gram oil gave 0.1735 gram H_2O and 0.6805 gram CO_2.

	Calculated for $C_{11}H_{14}O_2$.	Found. I.	II.
C	74.16	74.04	74.03
H	7.86	7.87	7.69

Paraisobutylsalicyl aldehyde, $C_6H_3\begin{cases}OH & (1)\\ COH & (2)\\ C_4H_9 & (4)\end{cases}$, is a yellow, highly refracting oil with an aromatic odor resembling that of

salicylic aldehyde. It boils at 251°–252° at 729 mm. pressure with slight decomposition, and does not solidify at —18°. Its specific gravity at 20° is 1.039. It is easily soluble in ordinary organic solvents. With ferric chloride it gives a violet coloration. From the neutral solution of the sodium salt, copper sulphate throws down a yellowish-green precipitate. Silver nitrate, lead acetate, calcium chloride and barium chloride give white precipitates.

Paraisobutylsalicyl hydrazone, $C_6H_3\begin{cases}OH\\CH:N.NHC_6H_5\\C_4H_9\end{cases}$, has been mentioned before. It is formed whenever the aldehyde and phenylhydrazine are mixed alone or in solution.

Analysis of substance crystallized from petroleum-ether and then dried at 100°—it burns with great difficulty:

0.2427 gram substance gave 0.1700 gram H_2O and 0.6793 gram CO_2.

	Calculated for $C_{17}H_{20}N_2O$.	Found.
C	76.12	76.32
H	7.46	7.78

0.1939 gram substance dissolved in 16.07 grams benzene gave 0.225° depression.

Molecular weight found, 262; theory requires 268.

Paraisobutylsalicyl hydrazone crystallizes from alcohol or petroleum-ether in thin, golden, monoclinic plates, easily soluble in ether, benzene, carbon bisulphide, chloroform, hot alcohol and hot petroleum-ether; slightly soluble in hot caustic soda. It melts at 178°.

Diacetylparaisobutylsalicyl hydrazone, $C_6H_3\begin{cases}OCOCH_3\\CH:N.N<\begin{matrix}COCH_3\\C_6H_5\end{matrix}\\C_4H_9\end{cases}$.—This was obtained by boiling the hydrazone for a short time with an excess of acetic anhydride. The product, poured into water, separated out as an oil which soon solidified. It was purified by washing with dilute alkali and crystallizing from dilute alcohol.

Analysis.

I. 0.2180 gram substance gave 0.1364 gram H_2O and 0.5724 gram CO_2.

II. 0.2622 gram substance gave 0.1629 gram H_2O and 0.7504 gram CO_2.

	Calculated for $C_{21}H_{24}N_2O_4$.	Found. I.	II.
C	71.59	71.60	71.54
H	6.82	6.95	6.90

0.1716 gram substance dissolved in 14.074 grams glacial acetic acid gave a depression of 0.13°.

Molecular weight found, 362; theory requires 352.

The diacetyl compound crystallizes in small white needles melting at 128°. It is easily soluble in organic solvents.

Paraisobutylsalicylidene aniline, $C_6H_3\begin{cases}OH\\CH:N.C_6H_5\\C_4H_9\end{cases}$ — Equal molecules of *p*-isobutylsalicyl aldehyde and aniline were warmed gently in a test-tube. Water was given off, and on cooling the mixture solidified. It was purified by crystallization from alcohol and petroleum-ether.

Analysis.

0.3 gram substance gave 15 cc. N at 20° and 730 mm.

	Calculated for $C_{17}H_{19}NO$.	Found.
N	5.53	5.51

This compound crystallizes in yellow monoclinic plates that exhibit pleochroism and melt at 87°. It is easily soluble in ether, alcohol, benzene, and chloroform; less so in petroleum-ether. Warmed with dilute acids or alkalies it is decomposed into aniline and aldehyde.

Paraisobutylsalicyl aldoxime, $C_6H_3\begin{cases}OH\\CH:N.OH\\C_4H_9\end{cases}$ — Paraisobutylsalicyl aldehyde was dissolved in dilute alcohol together with slightly more than the calculated quantity of hydroxylamine hydrochloride, and enough sodium carbonate to decompose the latter. After standing over night the alcohol was distilled off, the residue acidified with hydrochloric acid and poured into water. The oxime was deposited in fine acicular crystals. The yield is nearly quantitative. The substance will not crystallize from alcohol, but separates out as an oil. From petroleum-ether it crystallizes in long monoclinic needles melting at 112°.

Analysis.

I. 0.2 gram substance gave 0.1404 gram H_2O and 0.5004 gram CO_2.

II. 0.4 gram substance gave 28.3 cc. N at 22° and 722 mm.

	Calculated for $C_{11}H_{13}NO_2$.	Found. I.	II.
C	68.38	68.24	...
H	7.77	7.80	...
N	7.25	...	7.64

The oxime gives with ferric chloride a purple color. With Fehling's solution it forms a white precipitate, which on boiling is reduced to cuprous oxide. Warmed with mineral acids it is decomposed.

The oxime is soluble in hot water, insoluble in cold; soluble also in ether, benzene, and chloroform.

Dibenzoyl ester of paraisobutylsalicyl aldoxime, $C_6H_3\begin{cases}OCOC_6H_5\\ CH:N.OCOC_6H_5\\ C_4H_9\end{cases}$.—1.7 grams of the oxime were dissolved in sodium hydrate and 3 grams benzoyl chloride added; there separated out a heavy solid precipitate which was purified by crystallization from alcohol.

Analysis.

0.2 gram substance gave 0.1039 gram H_2O and 0.5475 gram CO_2.

	Calculated for $C_{25}H_{23}NO_4$.	Found.
C	74.81	74.65
H	5.74	5.77

The compound separates from hot alcohol in fine white monoclinic crystals that melt at 160°. It is difficultly soluble in hot alcohol, moderately soluble in light-boiling petroleum, and easily soluble in chloroform, ether, benzene, and carbon bisulphide.

The action of acetic anhydride upon the aldoxime.—8 grams of paraisobutylsalicyl aldoxime and 25 grams of acetic anhydride were boiled for eight (8) hours in a flask fitted with a condenser. This product was distilled directly. After the excess of acetic anhydride had been driven off the mercury rose rapidly, and there passed over between 287°–292° a light yellow oil insoluble in caustic potash.

Analysis.

0.2008 gram oil gave 0.1259 gram H_2O and 0.5300 gram CO_2.

	Calculated for $C_{13}H_{15}NO_2$.	Found.
C	71.98	71.89
H	6.96	6.91

The acetyl ether of *p*-isobutylsalicylonitrile, $C_6H_3\begin{cases}OCOCH_3\\CN\\C_4H_9\end{cases}$, formed by the removal of a molecule of water from the aldoxime, is a light yellow oil insoluble in water, easily soluble in organic solvents. The acetyl group is removed with great ease; alcohol doing so partially.

It was saponified by boiling with alcoholic potash. On evaporating off the alcohol and acidifying with dilute hydrochloric acid, the nitrile separates out as an oil which quickly solidifies. It was dried on a porous plate and purified by crystallizing from petroleum-ether.

Analysis.

0.2 gram substance gave 0.1347 gram H_2O and 0.5520 gram CO_2.

	Calculated for $C_{11}H_{13}NO$.	Found.
C	75.43	75.28
H	7.43	7.48

Paraisobutylsalicylonitrile, $C_6H_3\begin{cases}OH\ (1)\\CN\ (2)\\C_4H_9\ (4)\end{cases}$, crystallizes from petroleum-ether—in which it is difficultly soluble—in fine white monoclinic needles. The angle β is 87° 15′.

It is soluble in hot water, alcohol, benzene, chloroform, and ether; insoluble in cold water.

Methyl ether of paraisobutylsalicyl aldehyde, $C_6H_4\begin{cases}OCH_3\\COH.\\C_4H_9\end{cases}$—

9 grams of the aldehyde were dissolved in absolute methyl alcohol to which enough sodium had been added to form the sodium salt of the aldehyde. The mixture was heated on a water-bath for six hours with an excess of methyl iodide.

After distilling off the excess of methyl alcohol and methyl iodide, the residue was treated with water and extracted with ether. After drying the ethereal solution and distilling off the ether, the bulk of the residual oil passed over between 274°–276° at 735 mm. pressure.

Analysis.

0.2438 gram oil gave 0.6705 gram CO_2 and 0.1835 gram H_2O.

	Calculated for $C_{12}H_{14}O_2$.	Found.
C	75.00	75.01
H	8.33	8.36

The methyl ether forms a clear yellow, strongly refracting oil, insoluble in water, soluble in organic solvents.

Equal molecules of the methyl ether and hydroxylamine hydrochloride were dissolved in dilute alcohol with the proper amount of sodium carbonate. The solution was allowed to stand over night. On distilling off the alcohol, acidifying the residue and extracting the solution with ether, there was obtained a thick oil. This was purified by solution in caustic soda and reprecipitation. It was dried at 90° in an air-bath and over sulphuric acid.

Analysis.

0.2575 gram oil gave 0.1893 gram H_2O and 0.6557 gram CO_2.

	Calculated for $C_{13}H_{17}NO_2$.	Found.
C	69.56	69.44
H	8.22	8.11

The oxime of the methyl ether of paraisobutylsalicyl aldehyde, $C_6H_3\begin{cases}OCH_3\\ CH:N.OH\\ C_4H_9\end{cases}$, forms a thick oil that will not crystallize. It is soluble in ordinary solvents and caustic alkalies.

Benzyl ether of paraisobutylsalicyl aldehyde, $C_6H_3\begin{cases}OC_7H_7\\ COH\\ C_4H_9\end{cases}$.—The dry sodium salt of the aldehyde was suspended in benzene and boiled for several hours with a slight excess of benzyl chloride. The benzene was then filtered from the sodium chloride and allowed to evaporate. The solid that separated out was dried on a porous plate and crystallized from methyl alcohol.

Analysis.

0.2 gram substance gave 0.1387 gram H_2O and 0.5895 gram CO_2.

	Calculated for $C_{18}H_{20}O_2$.	Found.
C	80.60	80.38
H	7.46	7.70

From methyl alcohol the ether crystallizes out in long slender monoclinic prisms with a fracture parallel to the basal cleavage. It is easily soluble in organic solvents and melts at 70°–71°.

Ethylcarbonic ether of paraisobutylsalicyl aldehyde,

C_6H_3—$\begin{cases} OCOOC_2H_5 \\ COH \\ C_4H_9 \end{cases}$.—This was made by the action of ethyl chlorformate on the dry sodium salt of the aldehyde in carbon-bisulphide solution. The small quantity of product obtained was difficult to purify. Finally it was distilled and a light yellow oil obtained. This after standing for several weeks in a desiccator partially solidified. The crystals were washed with petroleum-ether, dried on a plate and over sulphuric acid and analyzed.

0.1190 gram substance gave 0.0767 gram H_2O and 0.2897 gram CO_2.

	Calculated for $C_{14}H_{18}O_4$.	Found.
C	67.20	67.30
H	7.20	7.16

The ether melts at 63°.

Action of acetyl chloride upon paraisobutylsalicyl aldehyde.—There was added to *p*-isobutylsalicyl aldehyde, in a test-tube fitted with an air condenser, half its volume of acetyl chloride. The mixture, which warmed up slightly, was allowed to stand for several hours and then gently heated to complete the reaction. The oil obtained on treating with a little alcohol to decompose the excess of acetyl chloride, solidified. The yield is quantitative. The product was purified by crystallization from alcohol and petroleum-ether.

Analysis.

0.2453 gram substance gave 0.1656 gram H_2O and 0.7026 gram CO_2.

	Calculated for $C_{22}H_{26}O_3$.	Found.
C	78.10	78.05
H	7.69	7.50

0.3549 gram substance dissolved in 13.57 grams benzene gave a depression of 0.366°.

Molecular weight found, 350; theory requires 338.

Paradiisobutyldisalicyl aldehyde crystallizes from petroleum-ether in beautiful monoclinic needles that melt at 158°. It is easily soluble in alcohol, chloroform, ether, benzene, acetone,

carbon bisulphide, and acetic acid; insoluble in alkalies. On gently warming it dissolves in concentrated sulphuric acid with the formation of a deep red color. This when poured into water gives a quantitative yield of *p*-isobutylsalicyl aldehyde.

The quantitative formation of this condensation-product is a further proof of the fact already pointed out by Bradley and one of us, that a hydrocarbon group does not interfere with the condensation of orthohydroxy aldehydes with acetyl chloride.

The compound is a very stable one; boiling with a strong alkaline solution of potassium permanganate does not affect it.

Bromine derivatives of paraisobutylsalicyl aldehyde.—One molecule of the dry sodium salt was suspended in carbon bisulphide and one molecule of bromine added. The reaction was completed by heating on a water-bath. The solution was filtered from the sodium bromide, the carbon bisulphide distilled off, and the solid residue dried on a porous plate. It was then dissolved in alcohol; from this solution water precipitates a nearly pure product. It was further purified by crystallization from light boiling petroleum.

Analysis.

0.2030 gram substance gave 0.1491 gram AgBr.

	Calculated for $C_{11}H_{13}BrO_2$.	Found.
Br	31.13	31.25

Paraisobutylorthobromsalicyl aldehyde, $C_6H_2\begin{cases} OH & (1) \\ COH & (2) \\ C_4H_9 & (4) \\ Br & (6) \end{cases}$, crystallizes in large, slightly yellow monoclinic plates that exhibit pleochroism. The angle β is 71° 15′.

Its melting-point is 86°–87°. With ferric chloride it gives a violet color. When oxidized with potassium permanganate there is formed a crystalline product that melts at 208°. This is possibly the *p*-isobutyl-*o*-bromsalicylic acid, but the quantity obtained was too small for analysis.

Efforts to condense this bromaldehyde with the aid of acetyl chloride to a *p*-diisobutyl-*o*-dibromdisalicyl aldehyde were fruitless. No alkali-insoluble product could be obtained. This would seem to indicate that the presence of a negative bromine atom together with a hydrocarbon group will prevent condensation.

Paraisobutylorthobromsalicyl aldoxime, $C_6H_2\begin{cases}OH\\CH:N.OH\\C_4H_9\\Br\end{cases}$.—5 grams of the bromaldehyde were dissolved in alcohol and the calculated amounts of sodium carbonate and hydroxylamine hydrochloride added. After standing for 24 hours the reaction was complete, and the product was dried and crystallizes from a mixture of benzene and petroleum-ether. The yield is good.

Analysis.

0.2546 gram substance gave 0.1758 gram AgBr.

	Calculated for $C_{11}H_{14}BrNO_2$.	Found.
Br	29.41	29.38

The new body crystallizes in white, tabular, monoclinic plates that melt at 163°. It is easily soluble in ether, carbon bisulphide, hot alcohol, and hot benzene; difficultly soluble in cold alcohol, cold benzene, chloroform, or petroleum-ether.

Dibenzoyl ether of paraisobutylorthobromsalicyl aldoxime, $C_6H_2\begin{cases}O.CO.C_6H_5\\CH:N.OCOC_6H_5\\C_4H_9\\Br\end{cases}$.—1.25 grams of the bromaldoxime were dissolved in caustic soda and the calculated amount of benzoyl chloride added. The new compound separates out in hard lumps which are very difficultly soluble in the hot alcohol from which it was crystallized.

Analysis.

0.4220 gram substance gave 0.1642 gram AgBr.

	Calculated for $C_{25}H_{22}BrNO_4$.	Found.
Br	16.66	16.58

The compound crystallizes from hot alcohol in fine white monoclinic needles that melt at 189°.

It is easily soluble in benzene, chloroform, and carbon bisulphide; less so in ether and in light-boiling petroleum.

Paraisobutylorthobromsalicyl hydrazone, $C_6H_2\begin{cases}OH\\CH:N.NHC_6H_5\\C_4H_9\\Br\end{cases}$.—To an alcoholic solution of the bromaldehyde a little phenyl

hydrazine was added. The reaction goes slowly, but on standing there separate out the long needles of the hydrazone.

These were purified by crystallization from light-boiling petroleum.

Analysis.

0.2183 gram substance gave 0.1180 gram AgBr.

	Calculated for $C_{17}H_{19}BrN_2O$.	Found.
Br	23.05	23.00

The hydrazone forms long monoclinic crystals that melt at 152°. It is easily soluble in ether, chloroform, and benzene; moderately soluble in alcohol, and difficultly soluble in light-boiling petroleum.

The authors desire to thank Professor Erasmus Haworth of the University, who has very kindly identified for them the crystalline forms of some of the preceding compounds.

Contributions from the Chemical Laboratory of Cornell University.

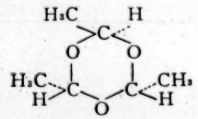
THE POLYMERIC MODIFICATIONS OF PROPIONIC ALDEHYDE: PARAPROPIONIC AND METAPROPIONIC ALDEHYDES.

By W. R. Orndorff and Miss L. L. Balcom.

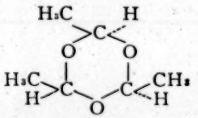
It has been shown in a previous paper[1] by one of us that the polymeric modifications of acetic aldehyde, paraldehyde and metaldehyde have the same molecular weight (three times that of the simple aldehyde), and that metaldehyde is the unstable form changing very readily into a mixture of paraldehyde and a solid product having a molecular weight four times that of the acetic aldehyde. In this paper attention was also called to the fact that paraldehyde and metaldehyde differ from each other only in their physical properties, such as solubility, crystal form, volatility, melting-point, etc., and that their entire chemical conduct could be accurately represented by the same structural for-

[1] This Journal 16, 43.

mula in a plane. These facts led to the idea that the two substances were stereoisomers, paraldehyde the stable form being best represented by the trans-formula and metaldehyde by the cis-formula:



Paraldehyde.[1]



Metaldehyde.[1]

These two formulas were then shown to be in accord with the entire conduct of the substances.

Polymerization, it is well known, is a characteristic property of the aldehydes, many of the well-known aldehydes occurring in polymeric modifications and some of them in more than one variety. Propionic aldehyde (C_2H_5CHO), for example, has been shown by one of us[2] to polymerize and form a parapropionic and a metapropionic aldehyde. The first product is a liquid which resembles paraldehyde very closely, the second is a solid analogous in every respect to metaldehyde. This resemblance being so striking, it was thought that perhaps these two substances were also stereoisomers, and that all aldehydes (with the exception of formic aldehyde) would be found to yield two isomeric trialdehydes which were stereoisomers. Parapropionic and metapropionic aldehydes were therefore made and carefully studied in order to determine their molecular weights and the relation existing between them and the simple propionic aldehyde from which both are made.

Parapropionic Aldehyde.

This substance was made from the *purest* propionic aldehyde by the polymerizing action of hydrochloric acid gas, the hydrochloric acid removed by means of dry barium carbonate, the product dried with calcium chloride and subjected to careful fractional distillation, using a Hempel distilling-bulb. The parapropionic aldehyde thus made and purified was found to boil, with slight decomposition into propionic aldehyde, at 169°–170° C. (uncorr.)

[1] The broken lines represent the groups below, the unbroken lines those above, the plane of the paper.

[2] This Journal **12**, 353.

and to solidify completely at —20° C. to a mass of needle-shaped crystals. A determination of its specific gravity showed that as compared with water at 4° C. its specific gravity at 0° C. is 0.9549. It is only very slightly soluble in water, though freely soluble in ether and alcohol. It resembles paraldehyde closely, having a very similar odor, and being converted into the simple aldehyde (propionic aldehyde) when distilled with a small quantity of sulphuric or hydrochloric acid. It reacts neither with fuchsine sulphurous acid nor with hydroxylamine, and hence does not contain the aldehyde group CHO.

Determinations of the molecular weight of parapropionic aldehyde by the cryoscopic method, using the Beckmann apparatus and thermometer, gave the following results:

Parapropionic aldehyde $(C_3H_6O)_3 = 174$. Solvent, phenol[1]; molecular depression, 75; depression coefficient, 0.4310.

Wt. Solvent.	Wt. Sub.	Concentr.	Depress.	Dep. Coef.	Mol. Dep.	Mol. Wt. found.
26.8345	0.2100	0.7826	0°.345	0.4408	76.7	170
	0.3445	1.2834	0°.565	0.4402	76.6	170
	0.5125	1.9099	0°.835	0.4372	76.0	172
26.8345	0.1360	0.5068	0°.220	0.4341	75.5	173
	0.2890	1.0770	0°.470	0.4364	75.9	172

These results show that the molecular weight of parapropionic aldehyde in solution in phenol is about 174 or three times that of propionic aldehyde (58), and that consequently its formula is $(C_3H_6O)_3$ or $C_9H_{18}O_3$.

In this connection it should be stated that S. Reformatsky[2] recently obtained parapropionic aldehyde by the action of zinc and ethyl monochloracetate on propionic aldehyde. Analyses of the substance showed that it had the formula $(C_3H_6O)_n$, and a vapor density determination by the Victor Meyer method in the vapor of boiling naphthalene gave its specific gravity as referred to air as 5.95, while that required by the formula $(C_3H_6O)_3$ is 6.02.

Metapropionic Aldehyde.

This substance was made according to the directions already given.[3] The substance is formed with much greater difficulty than

[1] The phenol used in these determinations was prepared from the c. p. article by distillation and melted at 41°–42° C. (uncorr.) In working with phenol care was taken to exclude moisture by means of the device already described. See this Journal **15**, 353.

[2] Jour. Russ. Chem. Soc. **22**, 197. [3] *Loc. cit.*

the metaldehyde, and unless the directions are carefully followed and the purest propionic aldehyde is used, the amount of metapropionic aldehyde formed is liable to be very small. The metapropionic aldehyde was filtered from the parapropionic aldehyde always formed simultaneously with the meta-product, washed with water, drained thoroughly, and dried first in the air on drying paper and then in a Hempel desiccator containing sulphuric acid.

The metapropionic aldehyde thus prepared resembles metaldehyde very closely, and like metaldehyde it is converted into the simple aldehyde from which it is derived, by heating with sulphuric or hydrochloric acid. With fuchsine sulphurous acid and with hydroxylamine it gives no reaction and hence does not contain the aldehyde group CHO.

Determinations of the molecular weight of the freshly prepared metapropionic aldehyde by the cryoscopic method, using the Beckmann apparatus and thermometer, gave the following results:

Metapropionic aldehyde, $(C_3H_6O)_3 = 174$. Solvent, phenol[1]; molecular depression, 75; depression coefficient, 0.4310.

Wt. Solvent.	Wt. Sub.	Concentr.	Depress.	Dep. Coef.	Mol. Dep.	Mol. Wt. found.
24.9265	0.1035	0.4152	0°.180	0.4335	75.4	173
	0.1910	0.7662	0°.320	0.4176	72.7	179
24.9265	0.0840	0.3370	0°.150	0.4451	77.4	169
	0.1445	0.5797	0°.255	0.4399	76.5	170
	0.2148	0.8613	0°.375	0.4354	75.7	172

These results certainly show that the freshly prepared metapropionic aldehyde has the same molecular weight (174) and the same formula as parapropionic aldehyde, viz. $(C_3H_6O)_3$.

After the metapropionic aldehyde had stood for some weeks at the temperature of the laboratory (about 22° C.) it was found to give a strong odor of the parapropionic aldehyde when powdered. Determinations of the molecular weight in solution in phenol of the solid product remaining (after the odor of parapropionic aldehyde had disappeared from the powdered product) gave the following results:

Metapropionic aldehyde, $(C_3H_6O)_3 = 174$; $(C_3H_6O)_4 = 232$. Solvent, phenol.

Wt. Solvent.	Wt. Sub.	Concentr.	Depress.	Dep. Coef.	Mol. Dep.	Mol. Wt. found.
21.4055	0.1000	0.4671	0°.160	0.3426	79.4	218
	0.1945	0.9086	0°.310	0.3412	79.1	219

[1] See footnote, page 647.

These results show that the molecular weight of this substance is intermediate between that required for the formula $(C_3H_6O)_3$ and $(C_3H_6O)_4$, and would seem to indicate that the solid product remaining is a mixture of a tetramolecular product $(C_3H_6O)_4$ and some of the unchanged metapropionic aldehyde.

After the metapropionic aldehyde had stood for about two months it was found to closely resemble metaldehyde that had stood for some time. The crystals, which had become dull and opaque, were much more easily powdered, and gave off at the same time a very strong odor of parapropionic aldehyde. Molecular weight determinations in solution in phenol gave the following results:

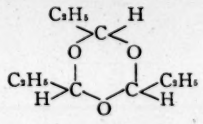
Solvent, phenol; $(C_3H_6O)_3 = 174$; $(C_3H_6O)_4 = 232$.

Wt. Solvent.	Wt. Sub.	Concentr.	Depress.	Dep. Coef.	Mol. Dep.	Mol. Wt. found.
27.3995	0.0836	0.3051	0°.105	0.3441	79.8	218
	0.1716	0.6263	0°.215	0.3433	79.6	218
	0.2441	0.8909	0°.305	0.3424	79.4	219

showing again a mixture of the tetrapropionic aldehyde $(C_3H_6O)_4$ and some of the unchanged meta-product.

Metapropionic aldehyde like metaldehyde then decomposes on standing into the para compound and a tetramolecular product, and is hence the unstable form. It should be noted, however, that metapropionic aldehyde does not decompose so readily as metaldehyde does.

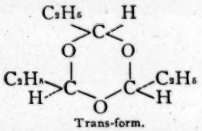
From these results it must be inferred that parapropionic aldehyde and the freshly made metapropionic aldehyde have the same molecular weight and the same empirical formula. Now as they both easily revert to the simple aldehyde by the action of the same reagents which bring about the polymerization of that aldehyde, and as neither contains the aldehyde group CHO, it is quite likely that the oxygen atoms here play the part of connecting atoms, and that both substances are to be represented by the same structural formula in a plane:



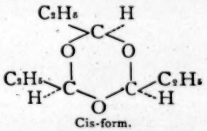
which formula is in strict accord with the entire chemical conduct of the two substances.

A careful study of the chemical conduct of these two substances leads inevitably to the conclusion that they are stereo-isomers. The simultaneous formation of both by the action of the same polymerizing agents on the simple aldehyde, the conversion of the metapropionic aldehyde into the para-product and the solid polymer, and the fact that the chemical conduct of both substances is absolutely identical with the same reagents, can only be explained on this assumption.

Referring to the structural formula, it will be seen more clearly by using models[1] that it admits of two configurations in space, and only two, as follows:



Trans-form.



Cis-form.

The trans-formula is generally assigned to the more stable modification, so that parapropionic aldehyde is probably best represented by that formula, while the less stable metapropionic aldehyde in all probability has the cis-formula.

Further work on the polymerization of the aldehydes and the relation between these polymeric modifications is in progress in this laboratory and will be reported on at an early date.

CORNELL UNIVERSITY CHEMICAL LABORATORY, *October*, 1894.

REVIEWS AND REPORTS.

SELECT METHODS IN CHEMICAL ANALYSIS. By WILLIAM CROOKES. Third edition, rewritten and enlarged.

The revised edition of this work will be welcomed by the many who have found the previous editions so useful in their laboratory practice. The work is so well known among chemists that an

[1] The Kekulé models are excellent for this purpose.

extended explanation of the author's object in writing it is unnecessary. The views and purposes which have guided him in the preparation of the last revision will be best presented by means of liberal quotations from the preface:

"A third edition of 'Select Methods in Chemical Analysis' having been called for, advantage has been taken to go over the whole work and remove some of the processes to make room for others which have been proposed and found to be successful during the eight years which have elapsed since the second edition was published. It must, however, not be assumed that the processes so discarded are of little value. Indeed, some are at the present time in constant use, having taken their position as regular laboratory processes, and have only been removed from these pages because their value is now too well known to make it advisable to retain them in a book which the author wishes to be looked upon as mainly a collection of novel or little-known processes. As soon as a new process takes its place among ordinary laboratory processes there is no reason for its retention here. Other processes have been omitted because further experience with them has shown the author that they are not so trustworthy as other newer processes which have taken their place. Others again have been omitted to prevent the book becoming of an unwieldy size. Thus most volumetric operations have been omitted, as there are now several standard works which are devoted to this branch of analysis. Then, mere detections which are not separations, and processes of only technical importance, have to a great extent been left out; the latter are well provided for in the technical literature. It has also been thought advisable to omit many purely assaying and furnace operations, as not exactly coming within the scope of the book and being more fully treated in special works on assaying. . . . .

"The space gained by these omissions has been partly filled up by new processes which the author has considered worth introducing; but chiefly it has been utilized in giving to the chemical world a series of electrical separations and other processes from the standard work of Dr. Classen. . . . .

"The author wishes to point out that this book is not to be looked upon as an encyclopædia of chemical analysis, in which is laid down every good method for the qualitative and quantitative examination of every known substance under every possible combination of circumstances. The author has merely given such methods as have been proved in his own laboratory. Others—possibly no less efficient—have been passed over because he cannot vouch personally for their value. A main object has been to bring into notice a number of little-known expedients and precautions which prevent mistakes, insure accuracy or economize time."

H. N. M.

QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS. By DR. ALEXANDER CLASSEN, Professor of Chemistry and Director of the Inorganic Laboratory in the Royal School of Technology at Aachen. Authorized translation. Second English from the third German edition. Revised and greatly enlarged by WILLIAM HALE HERRICK, A. M.

The work consists of three parts. Part I is general and treats of the various sources and the control of the current, and of the methods of determining and separating the individual metals. Part II is special, and deals with the analysis of alloys, minerals and metallurgical products. Part III contains tables designed to facilitate computation, directions for the preparation of reagents, and a record of analytical results. The original work is necessarily, to a very great extent, a record of the author's own valuable contributions to this branch of analytical chemistry, though the results and observations of others are not neglected. The claim upon the title-page of the translation, that the original has undergone a considerable enlargement, is scarcely warranted by the facts. The translator's contributions consist in the main of a description of the gravity cell, which is recommended as a substitute for the Daniell and the Meidinger; an account of the Paget thermopile, which, it appears, is more efficient than that of Clamond or of Noë; a brief discussion of the secondary battery; a description of Smith's current-reducer and Malapert's stand; and, finally, of some half a dozen references to the work of Smith and Knerr, and one to that of Chittenden and Blake. H. N. M.

LESSONS IN QUALITATIVE AND VOLUMETRIC CHEMICAL ANALYSIS FOR THE USE OF PHYSICIANS, PHARMACISTS AND STUDENTS. By DR. CHARLES O. CURTMAN, Professor of Chemistry in the Missouri Medical College, including LESSONS IN QUALITATIVE CHEMICAL ANALYSIS, by Prof. F. BEILSTEIN of St. Petersburg. Fourth edition, revised and enlarged, with many illustrations. John L. Boland Book Co., St. Louis. 1894.

In taking Professor Beilstein's book as basis of a manual for medical students, Prof. Curtman made a wise choice. Beilstein's method of training the beginner by the careful study of common salts and compounds is excellent. The student learns to think, to observe, and to remember, and to rely on his knowledge and memory rather than on a "table."

Prof. Curtman has built on the basis of Beilstein's manual in the same spirit. Organic compounds of particular interest to the medical student are carefully studied, and the reactions by which they can be detected are given. Among the substances studied we note salol, salicin, pyrogallol, acetanilid, antipyrin, other new organic remedies, and the vegetable alkaloids. The volumetric methods are the best in use. Particular attention is given to the analysis of drinking-water and to urine-analysis. This book can

be recommended as a valuable laboratory manual, and equally valuable as a book of reference for the physician, pharmacist, or chemical student. E. R.

A BRIEF INTRODUCTION TO QUALITATIVE ANALYSIS, FOR USE IN INSTRUCTION IN CHEMICAL LABORATORIES. By LUDWIG MEDICUS, Professor of Chemistry in the University of Würzburg. Translated from the fourth and fifth German editions, with additions, by JOHN MARSHALL, Assistant Professor of Chemistry in the Medical Department of the University of Pennsylvania. Third edition. Philadelphia: J. B. Lippincott Company, 1894.

The laboratory manual of Prof. Medicus has earned a widespread reputation as a good and thorough book of that school which trains the beginner largely through use of tables, in which the name, formula and appearance of the expected precipitate are described. Prof. Marshall has added to his translation new tables, including a table of solubilities, and has amplified the text to the extent of forty pages. E. R.

A MANUAL OF MICROCHEMICAL ANALYSIS. By PROF. H. BEHRENS, of the Polytechnic School in Delft, Holland. With an introductory chapter by PROF. JOHN W. JUDD, F. R. S., of the Royal College of Science, London. With 84 illustrations drawn by the author. Macmillan & Co., New York. $1.50.

Prof. Behrens' book is the first laboratory manual on this comparatively new branch of analysis, and is for this reason of great interest. In the first Part, the apparatus, the reagents, and the reactions of the single elements, are treated of. Numerous illustrations show the appearance of the crystalline precipitates as seen through the microscope.

In Part Second methods are given for the systematic analysis of water, ores, rocks, alloys, and combinations of rare elements. The chapter on the microchemical examination of rocks, first by study of slides, secondly by study of powdered rocks, is particularly valuable. Of almost equal interest and value is the chapter on iron and steel, on copper and its alloys, on the alloys of lead, tin, antimony, and on those of the precious metals. For petrographic research this manual is invaluable, but, to quote from Prof. Judd's introduction, "It is evident that these methods may be often employed with advantage in the ordinary chemical laboratory. . . . Archæologists and metallurgists, too, will find the methods for examining alloys of great service, especially in cases like those of manufactured articles or objects of art in which only very minute quantities of the material are available for analysis."

That Prof. Judd revised the manuscript of this book and wrote the introduction is in itself evidence of the value of the work.

E. R.

MANUAL OF PHYSICO-CHEMICAL MEASUREMENTS. By W. OSTWALD. Translated by J. WALKER. Macmillan & Co., 1894.

This laboratory manual, the original of which appeared about a year and a half ago (see this Journal **15**, 677), is now accessible to those who use only English. This work is not for the beginner, but, in the words of the author, "for the chemist or the physicist who has already gone through the greater part of his special course and recognizes the necessity of making himself acquainted with the borderland between the two sciences, which has of late attained to such importance." The subjects treated are: Calculation; measurement of length; weighing; measurement and regulation of temperature; thermostats; glass-blowing; measurement of pressure, volume and density; boiling-point; vapor-pressure; calorimetry; optical measurements; viscosity and surface-tension; solubility; determination of molecular weights in solutions; electrical measurements; chemical dynamics.

This English edition has appeared at a time when there is a growing interest manifested in physical chemistry, and it will doubtless contribute to work in this line in English and American laboratories. By accomplishing this the translator will have worked to good purpose.

The translation is admirable, being true to the original and at the same time written in clear and concise English. H. C. J.

LABORATORY MANUAL AND PRINCIPLES OF CHEMISTRY, FOR BEGINNERS. By GEORGE M. RICHARDSON, Associate Professor of Chemistry in the Leland Stanford Junior University. xii+233 pp. 12mo. New York: Macmillan & Co., 1894.

Dr. Richardson's book would perhaps be an ideal one in an ideal laboratory. He wishes to dispense with all teaching by text-book or lecture until the student has learned in the laboratory "the value of careful observation," "with such aid as he may get from his teacher for his chemical facts." It is a fair question to ask how long will this take: how long is the bewildered student to collect experimental data before he may be said to be in a position to be told the connection between his work and the facts of chemistry? In an ideal laboratory each student will have at his command ample room, all the apparatus desirable, unlimited time, and the constant attention of a thoroughly competent instructor. Under such conditions lectures and text-books are not necessary, nor are they desirable; but such conditions do not exist. As the world is at present, a student must be taught the reason for doing a given thing before he can be expected to do it well. A series of quantitative experiments requiring abundant time and carefully prepared—sometimes complicated—apparatus, is, in the experi-

ence of the present writer, of doubtful value when the very principles those experiments are intended to establish are as yet unknown to the student. It may be noticed that many of the quantitative experiments described belong strictly to an elementary course in physics and have no place here—not because they are not of great value, in fact essential, to a student of chemistry, but for the reason that every such student should have a good working knowledge of physics and should perform these experiments in connection with his physical course, especially as most chemical laboratories are not so arranged and equipped that such work can be done in them to proper advantage.

While fault may be found with Dr. Richardson's book on account of the character of the experiments described and of the order in which the various subjects are taken up, thoughtful teachers must in general commend the emphasis which he lays upon the value of laboratory work well performed. With this book as a laboratory manual supplemented by a *parallel* course of instruction in the fundamental facts of chemistry, excellent results should be obtained. The character of the experiments to be performed should then, of course, be varied somewhat to meet the capacity of the individual student. W. W. R.

AN ELEMENTARY MANUAL OF CHEMISTRY. By F. H. STORER and W. B. LINDSAY. Pp. 436, 8vo. The American Book Company, 1894.

This new revision of Eliot and Storer's Manual is an enlargement upon that of Prof. Nichols. One hundred pages have been added to the book; the number of experiments detailed has been increased and the work of recent years has been incorporated.

One or two points connected with the order in which the subjects treated of are taken up deserve, in the opinion of the present writer, adverse criticism. The Periodic Law is apparently not referred to until the last chapter in the book is reached. Again, the study of the hydrocarbons and their derivatives, "radicals" and constitutional formulæ, is taken up before the student has become acquainted with any of the metals and even before the salts of ammonium have been more than casually referred to. In this connection it may be noted that the statement on page 203, that the methyl group may be compared with "the group NH_4 (ammonia)" as similar "radicals," is probably a misprint.

The book is full—too full, many may think—of detailed fact, let alone hypothesis. Still, great care seems to have been exercised to make as clear a presentation of the subject as the space at hand would allow. W. W. R.

EINFÜHRUNG IN DAS STUDIUM DER QUALITATIVEN CHEMISCHEN ANALYSE. Von CARL FRIEDHEIM, Ph. D., Privat-Docent an der Universität Berlin. Berlin: Carl Habels Verlag, 1894. Pp. 335, 8vo.

Dr. Friedheim has written on the basis of Rammelsberg's "Leitfaden" a good and thorough elementary manual of qualitative analysis. The reactions of the metals and acids are more fully explained than is usual in such manuals: for example, he explains the behavior of the hydroxides of zinc, copper and nickel, and of silver oxide toward ammonia; the action of potassium cyanide on salts and sulphides, and similar points obscure to the beginner. For the student of chemistry in Germany, who hears lectures on inorganic chemistry in his first semester, and does not begin laboratory work till the second, the interval of time between lectures and laboratory tends to blunt the memory of the lecture—the more so as there are generally no stimulants provided in the form of our "quizzes," and no examinations till the "Doctor Examen." In the laboratory, qualitative analysis is taken up at once, without previous experiment in general chemistry. In the preface Dr. Friedheim deplores this state of things at length, and speaks openly of the ignorance of general chemistry shown by the average German student; he hopes that study of his book will better matters.

The present writer, from experience in teaching in Germany and here, endorses all that Dr. Friedheim says in his preface of the state of things in Germany, but is of the opinion that in the better American colleges general chemistry is so thoroughly taught, not only in lectures, but in laboratory, "quiz" and examination, that there is no need here of Dr. Friedheim's book. It is too large for a college student, too brief and too explanatory for a specialist. However, the book is written for German students, and it is to be hoped that it will gain entrance into many of the German university laboratories. E. R.

INORGANIC CHEMISTRY FOR BEGINNERS. By SIR HENRY ROSCOE, assisted by JOSEPH LUNT. Pp. 241, 12mo. New York: Macmillan & Co., 1894.

In this book the field is limited to the elements oxygen, hydrogen, nitrogen, chlorine, sulphur and carbon, and their most important compounds. At the same time the treatment is much fuller than in the author's well known "Lessons." The physical properties also of the substances dealt with are discussed with some degree of detail.

Professor Roscoe is still of the opinion that the instruction of a student in the elements of chemistry should *begin* with a consideration of the Atomic Theory. W. W. R.